Multigap superconductivity in centrosymmetric and noncentrosymmetric rhenium-boron superconductors

T. Shang, W. Xie, J. Z. Zhao, Y. Chen, D. J. Gawryluk, M. Medarde, M. Shi, H. Q. Yuan, E. Pomjakushina, and T. Shiroka

1Key Laboratory of Polar Materials and Devices (MOE), School of Physics and Electronic Science, East China Normal University, Shanghai 200241, China
2Center for Correlated Matter and Department of Physics, Zhejiang University, Hangzhou 310058, China
3Co-Innovation Center for New Energetic Materials, Southwest University of Science and Technology, Mianyang 621010, China
4Research Laboratory for Quantum Materials, Singapore University of Technology and Design, Singapore 487372, Singapore
5Laboratory for Multiscale Materials Experiments, Paul Scherrer Institut, CH-5232 Villigen, Switzerland
6Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen, Switzerland
7Laboratory for Muon-Spin Spectroscopy, Paul Scherrer Institut, CH-5232 Villigen, Switzerland
8Laboratorium für Festkörperphysik, ETH Zürich, CH-8093 Zürich, Switzerland

DOI: 10.1103/PhysRevB.103.184517

(Received 22 February 2021; revised 8 April 2021; accepted 13 May 2021; published 28 May 2021)

We report a comprehensive study of the centrosymmetric ReB and noncentrosymmetric Re2B1 superconductors. At a macroscopic level, their bulk superconductivity (SC), with \( T_c = 5.1 \text{ K} \) (ReB) and 3.3 K (Re2B1), was characterized via electrical-resistivity, magnetization, and heat-capacity measurements, while their microscopic superconducting properties were investigated by means of muon-spin rotation and relaxation (\( \mu\)SR). In both ReB and Re2B1, the low-\( T \) zero-field electronic specific heat and the superfluid density (determined via transverse-field \( \mu\)SR) suggest a nodeless SC. Both compounds exhibit some features of multigap SC, as evidenced by the temperature-dependent upper critical fields \( H_c^\alpha(T) \), as well as by electronic band-structure calculations. The absence of spontaneous magnetic fields below the onset of SC, as determined from zero-field \( \mu\)SR measurements, indicates a preserved time-reversal symmetry in the superconducting state of both ReB and Re2B1. Our results suggest that a lack of inversion symmetry and the accompanying antisymmetric spin-orbit coupling effects are not essential for the occurrence of multigap SC in these rhenium-boron compounds.

I. INTRODUCTION

The possibility to host unconventional and topological superconductivity (SC) or to act as systems to realize Majorana fermions [1–11] has made noncentrosymmetric superconductors (NCSCs) one of the most investigated materials in recent times. In NCSCs, a lack of inversion symmetry implies that admixtures of spin-singlet and spin-triplet superconducting pairings are allowed [1–3]. This sets the scene for a variety of exotic properties, such as upper critical fields beyond the Pauli limit [12,13], nodes in the superconducting gap [14–17], and multigap SC [18]. More interestingly, by using the muon-spin relaxation (\( \mu\)SR) technique, time-reversal symmetry (TRS) breaking has been observed to occur in the superconducting state of selected weakly correlated NCSCs. These include CaPtAs [17], LaNiC2 [19], La3T3 (\( T = \text{transition metal} \)) [20–22], Zr3Ir [23], and ReT3 [24–27]. Except for CaPtAs, where TRS breaking and superconducting gap nodes coexist below \( T_c \) [17,28], in most other cases the superconducting properties resemble those of conventional superconductors, characterized by a fully opened energy gap. In general, the causes behind TRS breaking in these superconductors are not yet fully understood and remain an intriguing open question.

To clarify the issue, \( \alpha\)-Mn-type ReT superconductors have been widely studied and demonstrated to show a superconducting state with broken TRS [24–27]. Our previous comparative \( \mu\)SR studies on Re-Mo alloys, covering four different crystal structures (including the noncentrosymmetric \( \alpha\)-Mn type), revealed that the spontaneous magnetic fields occurring below \( T_c \) were observed only in elementary rhenium and in Re0.88Mo0.12 [27,29,30]. By contrast, TRS was preserved in the Re-Mo alloys with a lower Re content (below \( \sim 88\% \)), independent of their centro- or noncentrosymmetric crystal structures [30]. Both elementary rhenium and Re0.88Mo0.12 adopting a simple centrosymmetric structure (hcp-Mg type) strongly suggests that a noncentrosymmetric structure is not essential in realizing TRS breaking in ReT superconductors. The \( \mu\)SR results for the Re-Mo family, as well as other \( \alpha\)-Mn-type superconductors, e.g., Mg10Ir19B16, Nb0.5Os0.5, Re2W, and Re2Ta [31–34], where TRS is preserved, clearly indicate that not only the Re presence but also its amount are crucial for the appearance and the extent of TRS breaking in ReT superconductors. How these results can be understood within a more general framework clearly requires further investigation.

Rhenium-boron compounds represent another suitable candidate system for studying the TRS breaking effects in the family of Re-based superconductors. Indeed, upon slight...
changes of the Re/B ratio, both centrosymmetric Re$_7$B$_3$ (C-Re$_7$B$_3$) and noncentrosymmetric Re$_7$B$_3$ (NC-Re$_7$B$_3$) compounds can be synthesized [35], the latter adopting the same Th$_7$Fe$_3$-type structure as La$_7$T$_3$ superconductors [20–22], which frequently exhibit broken TRS in the superconducting state. Although selected properties of Re$_7$B$_3$ and Re$_7$B$_3$ have been investigated by different techniques [36–38], their superconducting properties at a microscopic level, in particular, the superconducting order parameter, require further investigation.

In this paper, we report on a comprehensive study of the superconducting properties of Re$_7$B$_3$ and Re$_7$B$_3$ carried out via electrical-resistivity, magnetization, heat-capacity, and muon-spin rotation and relaxation measurements, as well as by electronic band-structure calculations. Our endeavors serve a dual purpose. First, since La$_7$T$_3$ shows evidence of TRS breaking below $T_c$, it is of interest to establish whether the isostructural Re$_7$B$_3$ compound also displays similar features. Second, by systematically investigating the C-Re$_7$B$_3$ and NC-Re$_7$B$_3$ superconductors, the previous findings regarding the Re$_7$B$_3$ family can be extended also to other NCSC families, thus providing further insight into the open question of TRS breaking in NCSCs.

II. EXPERIMENTAL AND NUMERICAL METHODS

Polycrystalline rhenium-boron compounds were prepared by arc melting Re (99.99%, ChemPUR) and B (99.995%, ChemPUR) powders with different stoichiometric ratios in a high-purity argon atmosphere. To improve the homogeneity, samples were flipped and remelted several times and, finally, annealed at 800°C for 2 weeks. The x-ray powder diffraction, measured using a Bruker D8 diffractometer with Cu $K\alpha$ radiation, confirmed the orthorhombic centrosymmetric structure of Re$_7$B$_3$ (Cmcm, No. 63) and the hexagonal noncentrosymmetric structure of Re$_7$B$_3$ (P6$_3$mc, No. 186; see details in Fig. S1 in the Supplemental Material [39]). The magnetization, electrical-resistivity, heat-capacity, and heat-capacity measurements were performed on Quantum Design magnetic property measurement system and physical property measurement system instruments, respectively. The bulk $\mu$SR measurements were carried out at the multipurpose surface-muon spectrometer (Dolly) of the Swiss muon source at Paul Scherrer Institut, Villigen, Switzerland. The $\mu$SR data were analyzed by means of the MUSRFIT software package [40].

The electronic band structures of Re$_7$B$_3$ and Re$_7$B$_3$ were calculated via density functional theory (DFT), within the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof realization [41], as implemented in QUANTUM ESPRESSO [42,43]. The projector augmented wave pseudopotentials were adopted for the calculation [44,45]. Electrons belonging to the outer atomic configuration were treated as valence electrons, here corresponding to 15 electrons belonging to the outer atomic configuration were treated as valence electrons, here corresponding to 15 elec-

III. RESULTS AND DISCUSSION

The bulk superconductivity of C-Re$_7$B$_3$ and NC-Re$_7$B$_3$ was first characterized by magnetic susceptibility measurements, using both field-cooled (FC) and zero-field-cooled (ZFC) protocols in an applied field of 1 mT. As indicated by the arrows in Fig. 1(a), a clear diamagnetic signal appears below the superconducting transition at $T_c = 5.1$ and 3.3 K for Re$_7$B$_3$ and Re$_7$B$_3$, respectively. After accounting for the demagnetization factor, the superconducting shielding fraction of both samples is close to 100%, indicative of bulk SC, which was further confirmed by heat-capacity measurements [39]. To determine the lower critical field $H_{c1}$, essential for performing $\mu$SR measurements on type-II superconductors, the field-dependent magnetization $M(H)$ was collected at various temperatures. Some representative $M(H)$ curves are shown in Figs. 1(c) and 1(d) for Re$_7$B$_3$ and Re$_7$B$_3$, respectively. The estimated $H_{c1}$ values as a function of temperature are summarized in Fig. 1(b), resulting in $\mu_0H_{c1}(0) = 5.4(1)$ mT and 7.8(1) mT for Re$_7$B$_3$ and Re$_7$B$_3$, respectively.

The upper critical field $H_{c2}$ of Re$_7$B$_3$ and Re$_7$B$_3$ was determined from measurements of the electrical resistivity, magnetization, and heat capacity under various magnetic fields up to 3 T (see Fig. S2 for details [39]). In zero magnetic field, the $T_c$ values determined using different methods are highly consistent. The upper critical fields are summarized in Figs. 2(a) and 2(b) versus the reduced superconducting transition temperature $T_c/T_c(0)$ for Re$_7$B$_3$ and Re$_7$B$_3$, respectively. $H_{c2}(T)$ was analyzed by means of Ginzburg-Landau (GL) [46], Werthamer-Helfand-Hohenberg (WHH) [47], and two-band (TB) models [48]. As shown in Fig. 2, both GL and WHH models can reasonably describe $H_{c2}(T)$ at low fields, i.e., $\mu_0H_{c2} < 0.5$ T (0.2 T) for Re$_7$B$_3$ (Re$_7$B$_3$). However, at higher magnetic fields, both models deviate significantly from the experimental data and provide underestimated $H_{c2}$ values. Such a discrepancy most likely hints at multiple superconducting gaps in Re$_7$B$_3$ and Re$_7$B$_3$, as evidenced also by the
positive curvature of $H_{c2}(T)$, a typical feature of multigap superconductors, as e.g., Lu$_2$Fe$_3$Si$_5$ [49], MgB$_2$ [50,51], and the recently reported Mo$_5$P$_2$B$_2$ [52]. Physically, the positive curvature reflects the gradual suppression of the small superconducting gap upon increasing the magnetic field. As clearly demonstrated in the insets of Fig. 2, $H_{c2}(T)$ values provide $\mu_0H_{c2}(0) = 3.5(1)$ and $1.05(5)$ T for Re$_3$B and Re$_7$B$_3$, respectively. The error bars refer to the superconducting transition widths $\Delta T_c$ in the specific-heat data.

To investigate at a microscopic level the SC of Re$_3$B and Re$_7$B$_3$, we carried out systematic transverse-field (TF) $\mu$SR measurements in an applied field of 20 mT, i.e., more than twice their $\mu_0H_{c2}(0)$ values [see Fig. 1(b)]. Representative TF-$\mu$SR spectra collected in the superconducting and normal states of Re$_3$B and Re$_7$B$_3$ are shown in Figs. 3(a) and 3(c), respectively. The additional field-distribution broadening due to the flux-line lattice (FLL) in the mixed state is clearly visible in Figs. 3(b) and 3(d), where the fast-Fourier transform (FFT) spectra of the corresponding TF-$\mu$SR data are presented. To describe the asymmetric field distribution (e.g., see FFT at 0.3 K), the TF-$\mu$SR spectra were modeled using

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

(1)

Here $A_i$, $A_{bg}$ and $B_i$, $B_{bg}$ are the asymmetries and local fields sensed by implanted muons in the sample and sample holder (copper, which normally shows zero muon-spin depolarization), $\gamma_\mu/2\pi = 135.53$ MHz/T is the muon gyromagnetic ratio, $\phi$ is a shared initial phase, and $\sigma_t$ is the Gaussian relaxation rate of the $i$th component. As shown by solid lines in Figs. 3(a) to 3(d), two oscillations (i.e., $n = 2$) are required to properly describe the TF-$\mu$SR spectra for both Re$_3$B and Re$_7$B$_3$. The derived $\sigma_t(T)$ as a function of temperature are summarized in the insets of Fig. 4. Above $T_c$, $\sigma_t(T)$ values are small and temperature independent, but below $T_c$ they start to increase due to the onset of FLL and the increased superfluid density. Simultaneously, a diamagnetic field shift appears below $T_c$, given by $\Delta B(T) = (B) - B_{appl}$, where $(B) = (A_1 B_1 + A_2 B_2)/A_{tot}$ and $A_{tot} = A_1 + A_2$, with $B_{appl}$ being the applied field. The effective Gaussian relaxation rate can be estimated from

$$\sigma_t^2/\gamma_\mu^2 = \sum_{i=1}^{2} A_i (\sigma_i^2/\gamma_\mu^2 + (B_i - (B))^2)/A_{tot} [53].$$

Considering the constant nuclear relaxation rate $\sigma_n$ in the narrow temperature range investigated here, confirmed also by zero-field (ZF) $\mu$SR measurements (see

---

**FIG. 2.** Upper critical fields $H_{c2}$ vs reduced temperature $T_c/T_c(0)$ for (a) Re$_3$B and (b) Re$_7$B$_3$, as determined from temperature-dependent electrical resistivity $\rho(T, H)$, magnetization $M(T, H)$, and heat capacity $C(T, H)$ and from field-dependent electrical resistivity $\rho(T, H)$. The contour plots of $\rho(T, H)$ in the insets indicate a clear positive curvature close to $T_c$. Three different models, including the GL (dash-dotted line), WHH (dashed line), and TB models (solid line), were used to analyze the $H_{c2}(T)$ data. Note the positive curvature visible near $\mu_0H \sim 0.5$ and 0.2 T for Re$_3$B and Re$_7$B$_3$, respectively. The error bars refer to the superconducting transition widths $\Delta T_c$ in the specific-heat data.

**FIG. 3.** (a) TF-$\mu$SR spectra of Re$_3$B collected in the superconducting (0.3 K) and normal (6 K) states in an applied magnetic field of 20 mT. (b) Fast Fourier transforms of the TF-$\mu$SR data shown in (a). (c) and (d) The analogous results for the Re$_7$B$_3$ case. The solid lines through the data are fits to Eq. (1), while the vertical dashed line marks the applied magnetic field. Note the clear diamagnetic shift and the field broadening at 0.3 K, as shown in (b) and (d). ZF-$\mu$SR spectra of (e) Re$_3$B and (f) Re$_7$B$_3$, collected in the superconducting and the normal states. Solid lines are fits using the equation described in the text. The overlapping data sets indicate no evident changes with temperature.
The superfluid density $\rho_{sc}$ vs the reduced $T/T_c$ is shown in Figs. 4(a) and 4(b) for Re$_3$B and Re$_7$B$_3$, respectively. The temperature-independent superfluid density below $T_c/3$ hints a fully gapped SC in both cases. Therefore, we analyzed $\rho_{sc}(T)$ by means of a fully gapped $s$-wave model:

$$
\rho_{sc}(T) = \frac{\lambda_{sc}^{-2}(T)}{\lambda_0^{-2}} = 1 + 2 \int_{\Delta(T)}^{\infty} \frac{\partial f}{\partial E} \frac{E dE}{\sqrt{E^2 - \Delta^2(T)}}. \tag{2}
$$

Here $f = (1 + e^{E/\gamma T})^{-1}$ and $\Delta(T)$ are the Fermi- and the superconducting-gap functions. $\Delta(T)$ is assumed to follow $\Delta(T) = \Delta_0 \tanh [1.82(1.108(T_c/T - 1))^{0.51}]$ [58], where $\Delta_0$ is the superconducting gap at 0 K. Since the upper critical field $H_{c3}(T)$ exhibits typical features of multigap SC (see Fig. 2), the superfluid density was fitted using Eq. (2) with one and two gaps. In the two-gap case, $\rho_{sc}(T) = \rho_{sc}^A(T) + (1 - w)\rho_{sc}^B(T)$, with $\rho_{sc}^A$ and $\rho_{sc}^B$ being the superfluid densities related to the first ($\Delta^A$) and second ($\Delta^B$) gaps and $w$ being a relative weight. For Re$_3$B, both the one- and two-gap models show an almost identical goodness-of-fit parameter ($\chi^2 \sim 1.2$), reflected in two practically overlapping fitting curves in Fig. 4(a). For Re$_7$B$_3$, instead, the two-gap model ($\chi^2 \sim 1.1$) is slightly superior to the one-gap model ($\chi^2 \sim 2.2$) [see Fig. 4(b)]. For the two-gap model, in the Re$_3$B case, the derived zero-temperature magnetic penetration depth is $\lambda_0 = 263(2)$ nm, and the gap values are $\Delta^A_0 = 0.72(1)$ meV and $\Delta^B_0 = 0.87(2)$ meV, with a weight $w = 0.7$. In the Re$_7$B$_3$ case, the corresponding values are $\lambda_0 = 261(2)$ nm, $\Delta^A_0 = 0.35(1)$ meV, and $\Delta^B_0 = 0.57(2)$ meV, with $w = 0.27$. For the one-gap model, the gap values are $\Delta_0 = 0.77(2)$ and 0.50(2) meV for Re$_3$B and Re$_7$B$_3$, with the same $\lambda_0$ values as in the two-gap case.

Unlike in the clean-limit case [$\xi_0 \ll l_e$; see Eq. (2)], in the dirty limit, the BCS coherence length $\xi_0$ is much larger than the electronic mean-free path $l_e$. In the BCS approximation, the temperature-dependent superfluid density in the dirty limit is given by [59]

$$
\rho_{sc}(T) = \frac{\Delta(T)}{\Delta_0 \tanh \left( \frac{\Delta(T)}{2\Delta_0 T} \right)}, \tag{3}
$$

where $\Delta(T)$ is the same as in Eq. (2). For Re$_3$B, $\xi_0$ is larger than $l_e$ ($\xi_0/l_e \sim 7.7$); therefore, Re$_3$B belongs to the dirty limit. However, in Re$_7$B$_3$, $\xi_0$ is smaller than $l_e$ ($\xi_0/l_e \sim 0.3$); therefore, it belongs to the clean limit. For both compounds, $\xi_0$ and $l_e$ are not significantly different and exhibit similar magnitudes. Hence, both Eqs. (2) and (3) describe quite well the low-$T$ superfluid density and yield similar superconducting gaps (see Table 1).

To further support the indications of a multigap SC obtained from $H_{c3}$, we measured also the zero-field specific heat down to $T_c/3$. After subtracting the phonon contribution ($\beta T^2$ + $\delta T^4$) from the measured data, the obtained electronic specific heat divided by $\gamma_n$, i.e., $C_e/\gamma_n T$, is shown in Figs. 5(a) and 5(b) vs the reduced temperature $T/T_c$ for Re$_3$B and Re$_7$B$_3$, respectively. The superconducting-phase contribution to the entropy can be calculated following the BCS expression [59]:

$$
S(T) = -\frac{6\gamma_n}{\pi^2k_B} \int_0^\infty [f \ln f + (1 - f) \ln(1 - f)] d\epsilon, \tag{4}
$$

where $f = (1 + e^{\epsilon/\gamma T})^{-1}$, $\gamma_n$ is the electronic specific heat coefficient, $k_B$ is the Boltzmann constant, and $\epsilon$ is the energy. The terms $\Delta(T)$ and $\rho_{sc}(T)$ in Eqs. (2) and (3) play a role in determining the magnitude of the entropy. The $s$-wave model neglects the $\Delta(T)$ term, whereas the multigap models are more realistic. The entropy is a crucial parameter to determine the superconducting symmetry. The $s$-wave model has $\Delta(T) = 0$ and $\rho_{sc}(T) = \rho_{sc}^0$, whereas the multigap models have $\Delta(T) \neq 0$ and $\rho_{sc}(T) \neq \rho_{sc}^0$. The $s$-wave model is expected to provide a lower upper limit on the entropy, while the multigap models are expected to provide a higher upper limit. Therefore, the entropy can be used to test the validity of the $s$-wave model.
TABLE I. Normal- and superconducting-state properties of C-Re$_3$B and NC-Re$_7$B$_3$, as determined from electrical-resistivity, magnetization, specific-heat, and $\mu$SR measurements, as well as from electronic band-structure calculations. The London penetration depth $\lambda_L$, the effective mass $m^*$, carrier density $n_c$, BCS coherence length $\xi_0$, electronic mean free path $l_e$, Fermi velocity $v_F$, and effective Fermi temperature $T_F$ were estimated following the methods in Ref. [30].

| Property | Units | Re$_3$B | Re$_7$B$_3$ |
|----------|-------|---------|------------|
| Space group | $Cmcm$ | $P6\overline{3}mc$ | |
| Inversion center | Yes | No | |
| $\rho_0$ | $\mu\Omega$ cm | 68.0 | 18.5 |
| Residual resistivity ratio | | 1.9 | 5.8 |
| $T^*_{c_1}$ | K | 5.2 | 3.5 |
| $T^*_{c_2}$ | K | 5.1 | 3.3 |
| $T^c_{c}$ | K | 4.7 | 3.1 |
| $T^\mu_{SR}$ | K | 4.8 | 2.9 |
| $\mu_0H_{c1}$ | mT | 5.4(1) | 7.8(1) |
| $\mu_0H_{c2}$ | T | 3.5(1) | 1.05(5) |
| $\gamma_0$ | mJ/mol K$^2$ | 9.6(1) | 21.5(2) |
| $\Theta_0$ | K | 390(3) | 440(5) |
| $N(E_F)^c$ | states/eV f.u. | 4.1(1) | 9.1(1) |
| $N(E_F)^{\mu SR}$ | states/eV f.u. | 2.35 | 5.7 |
| $\Delta_{0}(C)$ | meV | 0.75(2) | 0.47(1) |
| $\Delta_{0}(\mu SR)^{clean}$ | meV | 0.77(2) | 0.50(2) |
| $\Delta_{0}(\mu SR)^{dirty}$ | meV | 0.66(2) | 0.44(1) |
| $\omega$ | | 0.7 | 0.27 |
| $\Delta_{0}(C)$ | meV | 0.69(2) | 0.32(1) |
| $\Delta_{0}(C)$ | meV | 0.79(2) | 0.50(1) |
| $\Delta_{0}(\mu SR)^{clean}$ | meV | 0.72(1) | 0.35(1) |
| $\Delta_{0}(\mu SR)^{dirty}$ | meV | 0.87(2) | 0.57(2) |
| $\lambda_0$ | nm | 263(2) | 261(2) |
| $\lambda_{0}(eV)$ | nm | 353(4) | 259(2) |
| $\xi(0)$ | nm | 9.7(1) | 17.7(4) |
| $\kappa$ | | 36(1) | 14.6(5) |
| $\lambda_L$ | nm | 90(5) | 229(2) |
| $l_e$ | nm | 2.2(1) | 22(1) |
| $\xi_0$ | nm | 17(1) | 6.4(1) |
| $\xi_0/l_e$ | | 7.7 | 0.3 |
| $m^*$ | $m_e$ | 7.0(2) | 10.4(1) |
| $n_c$ | $10^{20}$ m$^{-3}$ | 2.4(3) | 0.56(1) |
| $v_F$ | $10^5$ m/s | 1.5(1) | 0.61(1) |
| $T_F$ | $10^3$ K | 1.0(1) | 0.25(1) |

where $f$ is the same as in Eq. (2). Then, the temperature-dependent electronic specific heat below $T_c$ can be obtained from $C_e(T) = \frac{\partial^2F}{\partial T^2}$, where $F$ is the Fermi-Dirac distribution function. The dash-dotted lines in Fig. 5 represent fits of an s-wave model with $\Delta_0 = 9.6(1)$ and $21.5(2)$ mJ/mol K$^2$ and a single gap $\Delta_0 = 0.75(2)$ and 0.47(1) meV for Re$_3$B and Re$_7$B$_3$, respectively. For Re$_7$B$_3$, the one-gap model reproduces the data for $T/T_c \gtrsim 0.5$, it deviates from them at lower temperatures, hence yielding a slightly larger $\chi^2 = 7.8$ than the two-gap model (see below). On the contrary, the two-gap model exhibits better agreement with the experimental data. The solid line in Fig. 5(b) is a fit with two energy gaps, i.e., $C_e(T) = \frac{\partial^2F}{\partial T^2}$. The dash-dotted lines in the insets are fits to $C/T = \gamma_0 + \beta T^2 + \Delta^2 T^2$ for $T > T_c$, while the dash-dotted and solid lines in the main panel represent the electronic specific heat calculated by considering a fully gapped s-wave model with one and two gaps, respectively.

Further evidence of the multigap SC and insight into the electronic properties of Re$_7$B$_3$ comes from band-structure calculations. The electronic band structures and the density of states (DOS) are shown in Fig. 6. As can be seen from Figs. 6(a) and 6(b), 4 and 12 different bands cross the Fermi level in Re$_3$B and Re$_7$B$_3$, respectively. Close to $E_F$, the DOS of both compounds is dominated by the Re 5$d$ orbitals, while the contribution from the Re 5$d$ orbitals is negligible (see Figs. 6(a) and 6(b) and Fig. S4 [39]). Away from the Fermi level, the Re 5$d$ and B 2$p$ orbitals are highly hybridized. The estimated DOS at $E_F$ are $\sim 4.7$ and $\sim 11.4$ states/(eV u.c.) for Re$_3$B and Re$_7$B$_3$, both comparable to the experimental values determined from the electronic specific-heat coefficient (see...
Table I). We expect the multigap features of Re\textsubscript{3}B and Re\textsubscript{7}B\textsubscript{3} to be closely related to the different site symmetries of Re atoms in the unit cell. For Re\textsubscript{3}B, according to band-structure calculations, the contribution of Re\textsubscript{1} (8f) atoms to the DOS is comparable to that of Re\textsubscript{2} (4c) atoms [see Figs. 6(c)]. However, for Re\textsubscript{7}B\textsubscript{3}, the contributions of Re\textsubscript{2} (6c) and Re\textsubscript{3} (6c) atoms are preponderant compared to that of Re\textsubscript{1} (2b) atoms.

Now, let us compare the superconducting parameters of Re\textsubscript{3}B and Re\textsubscript{7}B\textsubscript{3} with those of other superconductors. First, by using the SC parameters obtained from the measurements presented here, we calculated an effective Fermi temperature \(T_F = 1.0(1) \times 10^4\) and 0.25(1) \(\times 10^4\) K for Re\textsubscript{3}B and Re\textsubscript{7}B\textsubscript{3} (see other parameters in Table I). \(T_F\) is proportional to \(n_s^{-2/5}/m^*\), where \(n_s\) and \(m^*\) are the carrier density and the effective mass. Consequently, the different families of superconductors can be classified according to their \(T_c/T_F\) ratios into a so-called Uemura plot [60]. Several types of unconventional superconductors, including heavy fermions, organics, high-\(T_c\) iron pnictides, and cuprates, all lie in a 10\(^{-2}\) < \(T_c/T_F\) < 10\(^{-1}\) band (gray region in Fig. S5 [39]). Conversely, many conventional superconductors, such as, Al, Sn, and Zn, are located at \(T_c/T_F \lesssim 10^{-4}\). Between these two categories lie several multigap superconductors, e.g., LaNiC\textsubscript{2}, Nb\textsubscript{3}Ir\textsubscript{3}O, ReBe\textsubscript{22}, NbSe\textsubscript{3}, and MgB\textsubscript{2} [60–64]. Although there is no conclusive evidence for them to be classified as unconventional superconductors, the rhenium-boron superconductors lie clearly far off the conventional band. For Re\textsubscript{3}B, \(T_c/T_F = 4.8 \times 10^{-4}\) is almost identical to the analogous value for multigap ReBe\textsubscript{22} and LaNiC\textsubscript{2}, the latter representing a typical example of NCSCs. However, for Re\textsubscript{7}B\textsubscript{3}, \(T_c/T_F = 1.16 \times 10^{-3}\) is very close to the multigap Nb\textsubscript{3}Ir\textsubscript{3}O and elementary rhenium superconductors [27,30,63], the latter showing a breaking of TRS in the superconducting state and exhibiting a centrosymmetric crystal structure. In general, most of the weakly correlated NCSCs, e.g., Re\textsubscript{T}, Mo\textsubscript{3}Al\textsubscript{5}C, Li\textsubscript{2}(Pd, Pt)\textsubscript{3}B, and LaNiC\textsubscript{2}, exhibit \(T_c/T_F\) values between the unconventional and conventional bands [64], and this is also the case for Re\textsubscript{7}B\textsubscript{3}.

Second, we discuss why the multigap feature is more prominent in Re\textsubscript{7}B\textsubscript{3} than in Re\textsubscript{3}B, both in the temperature-dependent superfluid density and in the zero-field electronic specific heat. In general, if the weight of the second gap is relatively small and the gap sizes are not significantly different, it is difficult to discriminate between single- and two-gap superconductors based on temperature-dependent superconducting properties. For Re\textsubscript{3}B, the weight of the second gap \(w = 0.3\) is similar to that of Re\textsubscript{7}B\textsubscript{3} (\(w = 0.27\)). However, the gap sizes are clearly distinct in Re\textsubscript{7}B\textsubscript{3} (\(\Delta_f/\Delta_t \sim 0.6\)) compared to Re\textsubscript{3}B (\(\Delta_f/\Delta_t \sim 0.9\)). As a consequence, the multigap feature is more evident in Re\textsubscript{7}B\textsubscript{3}. On the other hand, from the analysis of \(H_2(T)\) using a two-band model, the derived interband and intraband couplings are \(\lambda_{12} = 0.08\) and \(\lambda_{11} \sim \lambda_{22} = 0.4\) and \(\lambda_{12} = 0.01\) and \(\lambda_{11} \sim \lambda_{22} = 0.15\) for Re\textsubscript{3}B and Re\textsubscript{7}B\textsubscript{3}, respectively. In both cases, the interband coupling is much smaller than the intraband coupling. In addition, the interband coupling of Re\textsubscript{3}B (0.08) is larger than that of Re\textsubscript{7}B\textsubscript{3} (0.01). In such situation, the SC gaps open at different electronic bands, making the multigap features less distinguishable in the former case [65]. Despite these differences, the underlying multigap SC feature of both samples is reflected in their upper critical fields \(H_c2(T)\) (see Fig. 2). To get further insight into the multigap SC of Re\textsubscript{3}B and Re\textsubscript{7}B\textsubscript{3}, the measurements of the field-dependent superconducting Gaussian relaxation rate \(\sigma_{sc}(H)\) and of the electronic-specific heat coefficient \(\gamma(H)\) provide a possible alternative, with both data sets being expected to show a distinct field response compared to a single-gap superconductor [52,61]. For example, \(\gamma(H)\) exhibits a clear change in slope when the applied magnetic field suppresses the small gap, a feature recognized as the fingerprint of multigap superconductors. Conversely, \(\gamma(H)\) is mostly linear in the single-gap case.

Finally, we discuss the effects of the lack of inversion symmetry in Re\textsubscript{7}B\textsubscript{3}. In NCSCs, the occurrence of admixture of singlet and triplet pairings is allowed, whose mixing degree is generally believe to be related to the strength of the antisymmetric spin orbit coupling (ASOC) [1] and, thus, to unconventional SC. Here, by comparing NC-Re\textsubscript{7}B\textsubscript{3} with C-Re\textsubscript{3}B, we find that a noncentrosymmetric structure and its accompanying ASOC have little effect on the superconducting properties of Re\textsubscript{7}B\textsubscript{3}. First, the upper critical field of NC-Re\textsubscript{7}B\textsubscript{3} is three times smaller than that of C-Re\textsubscript{3}B; in both cases \(H_c2\) is well below the Pauli limit. Second, according to the ZF-\(\mu\)SR data (Fig. 3), TRS is preserved in the superconducting states of both samples. The results presented here further support the idea that the presence of rhenium and its amount are the two key factors which determine the appearance of TRS breaking in Re-based superconductors, while the noncentrosymmetric structure plays only a marginal role. Obviously, the Re content in both Re\textsubscript{3}B and Re\textsubscript{7}B\textsubscript{3} might be below a certain threshold value, e.g., 88% in Re-Mo alloys [30]. Therefore, it could be interesting to check, upon increasing the Re content, whether the TRS breaking effect will appear also in rhenium-boron superconductors and, if so,
at which threshold value. Third, both Re$_7$B$_3$ and Re$_3$B exhibit nodeless SC with multiple gaps. In the case of Re$_7$B$_3$, whether the multigap feature is due to the band splitting caused by the ASOC or to the multiple bands crossing its Fermi level (the latter, in principle, accounting also for the C-Re$_3$B case) requires further theoretical work. Overall, as can be seen from Fig. 6(b), the ASOC and the band splitting are relatively small in Re$_7$B$_3$. Hence, we expect the spin-singlet pairing to be dominant in both the centrosymmetric and noncentrosymmetric rhenium-boron superconductors.

IV. CONCLUSION

To summarize, we studied the superconducting properties of the centrosymmetric Re$_3$B and noncentrosymmetric Re$_7$B$_3$ superconductors by means of electrical resistivity, magnetization, heat-capacity, and μSR techniques, as well as via numerical calculations. The superconducting states of Re$_3$B and Re$_7$B$_3$ are characterized by $T_c = 5.1$ and 3.3 K, and upper critical fields $H_{c2}(0) = 3.5$ and 1.05 T, respectively. The temperature-dependent zero-field electronic specific heat and superfluid density reveal a nodeless superconductivity, well described by an isotropic s-wave model. Both Re$_3$B and Re$_7$B$_3$ exhibit a positive curvature in their temperature-dependent upper critical field $H_{c2}(T)$, an established fingerprint of multigap superconductors. By combining our extensive experimental results with numerical band-structure calculations, we provided evidence of multigap superconductivity in both centro- and noncentrosymmetric rhenium-boron superconductors. Finally, the lack of spontaneous magnetic fields below $T_c$ indicates that, unlike in ReT or elementary rhenium, the time-reversal symmetry is preserved in the superconducting state of both Re$_3$B and Re$_7$B$_3$. Our results suggest the spin-singlet paring channel to be dominant in rhenium-boron superconductors.

Note added. After the present manuscript was submitted, a related work by Sharma et al. [66] appeared, in which similar compounds were studied via the μSR technique.

ACKNOWLEDGMENTS

This work was supported by the start funding from East-China Normal University (ECNU), Swiss SNF Grants No. 200021-169455 and No. 206021-139082, and the Sino-Swiss Science and Technology Cooperation (Grant No. IZLCZ2-170075). H.Q.Y. acknowledges support from the National Key R&D Program of China (Grants No. 2017YFA0303100 and No. 2016YFA0300202), the Key R&D Program of Zhejiang Province, China (Grant No. 2021C01002), and the National Natural Science Foundation of China (Grant No. 11974306). We acknowledge the allocation of beam time at the Swiss muon source.
the Noncentrosymmetric Superconductor CaPtAs, Phys. Rev. Lett. 124, 207001 (2020).

[18] S. Kuroiwa, Y. Saura, J. Akimitsu, M. Hiraishi, M. Miyazaki, K. H. Satoh, S. Takeshita, and R. Kadono, Multigap Superconductivity in Sesquicarbid es La$_2$C$_3$ and Y$_2$C$_3$, Phys. Rev. Lett. 100, 097002 (2008).

[19] A. D. Hillier, J. Quintanilla, and R. Cywinski, Evidence for Time-Reversal Symmetry Breaking in the Noncentrosymmetric Superconductor LaNiC$_2$, Phys. Rev. Lett. 102, 117007 (2009).

[20] J. A. T. Barker, D. Singh, A. Thamizhavel, A. D. Hillier, M. R. Lees, G. Balakrishnan, D. M. Paul, and R. P. Singh, Unconventional Superconductivity in La$_3$Ir$_2$ Revealed by Muon Spin Relaxation: Introducing a New Family of Noncentrosymmetric Superconductor That Breaks Time-Reversal Symmetry, Phys. Rev. Lett. 115, 267001 (2015).

[21] D. Singh, M. S. Scheurer, A. D. Hillier, D. T. Adroja, and R. P. Singh, Time-reversal symmetry breaking and unconventional pairing in the noncentrosymmetric superconductor La$_3$Rh$_3$, Phys. Rev. B 102, 134511 (2020).

[22] D. A. Mayoh, A. D. Hillier, G. Balakrishnan, and M. R. Lees, Evidence for the coexistence of time-reversal symmetry breaking and Bardeen-Cooper-Schrieffer-like superconductivity in La$_4$Pd$_4$, Phys. Rev. B 103, 024507 (2021).

[23] T. Shang, S. K. Ghosh, J. Z. Zhao, L.-J. Chang, C. Baines, M. K. Lee, D. J. Gawryluk, M. Shi, M. Medarde, J. Quintanilla, and T. Shiroka, Time-reversal symmetry breaking in the noncentrosymmetric Zr$_3$Ir superconductor, Phys. Rev. B 102, 020503(R) (2020).

[24] R. P. Singh, A. D. Hillier, B. Mazidian, J. Quintanilla, J. F. Annett, D. M. Paul, G. Balakrishnan, and M. R. Lees, Detection of Time-Reversal Symmetry Breaking in the Noncentrosymmetric Superconductor Re$_2$Zr using Muon-Spin Spectroscopy, Phys. Rev. Lett. 112, 107002 (2014).

[25] D. Singh, J. A. T. Barker, A. Thamizhavel, D. M. Paul, A. D. Hillier, and R. P. Singh, Time-reversal symmetry breaking in the noncentrosymmetric superconductor Re$_4$HF: Further evidence for unconventional behavior in the $\alpha$-Mn family of materials, Phys. Rev. B 96, 180501(R) (2017).

[26] T. Shang, G. M. Pang, C. Baines, W. B. Jiang, W. Xie, A. Wang, M. Medarde, E. Pompakushina, M. Shi, J. Mesot, H. Q. Yuan, and T. Shiroka, Nodeless superconductivity and time-reversal symmetry breaking in the noncentrosymmetric superconductor Re$_2$Ti$_3$, Phys. Rev. B 97, 020502(R) (2018).

[27] T. Shang, M. Smidman, S. K. Ghosh, C. Baines, L. J. Chang, D. J. Gawryluk, J. A. T. Barker, R. P. Singh, D. M. Paul, G. Balakrishnan, E. Pompakushina, M. Shi, M. Medarde, A. D. Hillier, H. Q. Yuan, J. Quintanilla, J. Mesot, and T. Shiroka, Time-Reversal Symmetry Breaking in Re-Based Superconductors, Phys. Rev. Lett. 121, 257002 (2018).

[28] W. Xie, P. R. Zhang, B. Shen, W. B. Jiang, G. M. Pang, T. Shang, C. Gao, M. Smidman, and H. Q. Yuan, CaPtAs: A new noncentrosymmetric superconductor, Sci. China: Phys., Mech. Astron. 63, 237412 (2020).

[29] T. Shang, D. J. Gawryluk, J. A. T. Verezhak, E. Pompakushina, M. Shi, M. Medarde, J. Mesot, and T. Shiroka, Structure and superconductivity in the binary Re$_{1-x}$Mo$_x$ alloys, Phys. Rev. Mater. 3, 024801 (2019).

[30] T. Shang, C. Baines, L.-J. Chang, D. J. Gawryluk, E. Pompakushina, M. Shi, M. Medarde, and T. Shiroka, Re$_{1-x}$Mo$_x$ as an ideal test case of time-reversal symmetry breaking in unconventional superconductors, npj Quantum Mater. 5, 76 (2020).

[31] A. A. Azcel, T. J. Williams, T. Goko, J. P. Carlo, W. Yu, Y. J. Uemura, T. Klimczuk, J. D. Thompson, R. J. Cava, and G. M. Luke, Muon spin rotation/relaxation measurements of the noncentrosymmetric superconductor Mg$_{10}$Ir$_{18}$B$_{16}$, Phys. Rev. B 82, 024520 (2010).

[32] D. Singh, J. A. T. Barker, A. Thamizhavel, A. D. Hillier, D. M. Paul, and R. P. Singh, Superconducting properties and $\mu$SR study of the noncentrosymmetric superconductor Nb$_{30}$Os$_{80.5}$, J. Phys.: Condens. Matter 30, 075601 (2018).

[33] P. K. Biswas, A. D. Hillier, M. R. Lees, and D. M. Paul, Comparative study of the centrosymmetric and noncentrosymmetric superconducting phases of Re$_3$W using muon spin spectroscopy and heat capacity measurements, Phys. Rev. B 85, 134505 (2012).

[34] J. A. T. Barker, B. D. Breen, R. Hanson, A. D. Hillier, M. R. Lees, G. Balakrishnan, D. M. Paul, and R. P. Singh, Superconducting and normal-state properties of the noncentrosymmetric superconductor Re$_3$Ta, Phys. Rev. B 98, 104506 (2018), and references therein.

[35] A. Kawano, Y. Mizuta, H. Takagiwa, T. Muranaka, and J. Akimitsu, The superconductivity in Re-B system, J. Phys. SOC. Jpn. 72, 1724 (2003).

[36] H. Takagiwa, A. Kawano, Y. Mizuta, T. Yamamoto, M. Yamada, K. Ohishi, T. Muranaka, J. Akimitsu, W. Higemoto, and R. Kadono, Magnetic penetration depth of a new boride superconductor Re$_3$B, Phys. B (Amsterdam, Neth.) 326, 355 (2003).

[37] C. S. Lue, Y. F. Tao, and T. H. Su, Comparative NMR investigation of the Re-based borides, Phys. Rev. B 78, 033107 (2008).

[38] K. Matano, S. Maeda, H. Sawaoaka, Y. Muro, T. Takabatake, B. Joshi, S. Ramakrishnan, K. Kawashima, J. Akimitsu, and G.-Q. Zheng, NMR and NQR studies on non-centrosymmetric superconductors Re$_3$B$_2$, LaBiPt, and BiPd, J. Phys. Soc. Jpn. 82, 084711 (2013).

[39] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.103.184517 for details on the measurements of crystal structure, electrical resistivity, magnetization, and heat capacity, as well as for the data analysis.

[40] A. Suter and B. M. Wojek, Musrfit: A free platform-independent framework for $\mu$SR data analysis, Phys. Procedia 30, 69 (2012).

[41] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77, 3865 (1996).

[42] P. Giannozzi et al., QUANTUM ESPRESSO: A modular and open-source software project for quantum simulations of materials, J. Phys.: Condens. Matter 21, 395502 (2009).

[43] P. Giannozzi et al., Advanced capabilities for materials modelling with Quantum ESPRESSO, J. Phys.: Condens. Matter 29, 465901 (2017).

[44] P. E. Blöchl, Projector augmented-wave method, Phys. Rev. B 50, 17953 (1994).

[45] A. D. Corso, Pseudopotentials periodic table: From H to Pu, Comput. Mater. Sci. 95, 337 (2014).

[46] X. Zhu, H. Yang, L. Fang, G. Mu, and H.-H. Wen, Upper critical field, Hall effect and magnetoresistance in the iron-based layered superconductor LaFeAsO$_{0.9}$F$_{0.1-\delta}$, Supercond. Sci. Technol. 21, 105001 (2008).

[47] N. R. Werthamer, E. Helfand, and P. C. Hohenberg, Temperature and purity dependence of the superconducting critical field.
Electron spin and spin-orbit effects, Phys. Rev. 147, 295 (1966).

Iron-based superconductors at high magnetic fields, Rep. Prog. Phys. 74, 124501 (2011), and references therein.

Two-band superconductivity featuring different anisotropies in the ternary iron silicide Lu2Fe5Sis, Phys. Rev. B 85, 174524 (2012).

The upper critical field in superconducting MgB2, J. Alloys Compd. 322, L10 (2001).

Very high upper critical fields in MgB2 produced by selective tuning of impurity scattering, Supercond. Sci. Technol. 17, 278 (2004).

Comparison of different methods for analyzing μSR line shapes in the vortex state of type-II superconductors, J. Phys.: Condens. Matter 21, 075701 (2009), and references therein.

Properties of the ideal Ginzburg-Landau vortex lattice, Phys. Rev. B 68, 054506 (2003).

The theory of the measurement of the London penetration depth in uniaxial type-II superconductors by muon spin rotation, Phys. C (Amsterdam, Neth.) 156, 515 (1988).

A stochastic model for low-field resonance and relaxation, in Magnetic Resonance and Relaxation: Proceedings of the XIVth Colloque Ampère, edited by R. Blinc (North-Holland, Amsterdam, 1967), pp. 810–823.

Muonic spin rotation, relaxation, and resonance: Applications to Condensed Matter (Oxford University Press, Oxford, 2011).