Nodeless superconductivity in the noncentrosymmetric Mo3Rh2N superconductor: A μSR study

T. Shang,¹,²,³,* Wensen Wei,⁴ C. Baines,⁵ J. L. Zhang,⁴ H. F. Du,³ M. Medarde,¹ M. Shi,² J. Mesot,³,⁶,⁷ and T. Shiroka⁷,⁶

¹Laboratory for Multiscale Materials Experiments, Paul Scherrer Institut, CH-5232 Villigen, Switzerland
²Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen, Switzerland
³Institute of Condensed Matter Physics, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
⁴Anhui Province Key Laboratory of Condensed Matter Physics at Extreme Conditions, High Magnetic Field Laboratory of the Chinese Academy of Sciences, Hefei 230026, People’s Republic of China
⁵Laboratory for Muon-Spin Spectroscopy, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
⁶Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
⁷Laboratorium für Festkörperphysik, ETH Zürich, CH-8093 Zurich, Switzerland

Nodeless superconductivity in the noncentrosymmetric Mo3Rh2N superconductor: A μSR study

Introduction. The current research interest in superconductivity (SC) involves either studies of high-temperature superconductors (such as cuprates or iron pnictides), or investigations of unconventional superconducting states. Superconductors with centrosymmetric crystal structures are bound to have either pure spin-singlet or spin-triplet pairings [1]. On the other hand, due to the relaxed space-symmetry requirement, noncentrosymmetric superconductors (NCSCs) may exhibit unconventional pairing [2,3]. A lack of inversion symmetry leads to internal electric-field gradients and hence to antisymmetric spin-orbit coupling (ASOC), which lifts the spin degeneracy of the conduction-band electrons. As a consequence, the superconducting order can exhibit a mixture of spin-singlet and spin-triplet pairings [2–4]. Of the many NCSCs known to date, however, only a few exhibit a mixed singlet-triplet pairing. Li2Pt3B and Li2Pd3B are two notable examples, where the mixture of singlet and triplet states can be tuned by modifying the ASOC through a Pd-for-Pt substitution [5,6]. Li2Pd3B behaves as a fully gapped s-wave superconductor, whereas the enhanced ASOC turns Li2Pt3B into a nodal superconductor, with typical features of spin-triplet pairing. Other NCSCs may exhibit unconventional properties besides mixed pairing. For instance, CePt3Si [7], CeIrSi3 [8], and K2Cr3As3 [9,10] exhibit line nodes in the gap, while others such as LaNi5C2 [11] and (La, Y)2C3 [12] show multiple nodeless superconducting gaps. In addition, due to the strong influence of ASOC, their upper critical fields can exceed the Pauli limit, as has been found in CePt3Si [13] and (TaNb)Rh2B2 [14]. Mo3Al2C forms a β-Mn-type crystal structure with space group P41/32. Muon-spin rotation/relaxation (μSR), nuclear magnetic resonance (NMR), and specific-heat studies have revealed that Mo3Al2C is a fully gapped, strongly coupled superconductor, which preserves time-reversal symmetry (TRS) in its superconducting state [15,16]. The recently synthesized Mo3Rh2N NCSC, a sister compound to Mo3Al2C, has been studied via transport and specific-heat measurements [17]. Yet, to date the microscopic nature of its SC remains largely unexplored. Density functional theory (DFT) calculations suggest a strong hybridization between the Mo and Rh 4d orbitals, reflecting the extended nature of the latter [18]. The density of states (DOS) at the Fermi level EF, arising from the Rh and Mo 4d orbitals, is comparable. This is in strong contrast with the Mo3Al2C case, where the DOS at EF is mostly dominated by Mo 4d orbitals [15,19]. In the Mo3Rh2N case, the SOC is significantly enhanced by the replacement of a light element, such as Al, with one with a strong SOC, such as Rh. Considering that already Mo3Al2C exhibits unusual properties [15,16], we expect the enhanced SOC to affect the superconducting properties of Mo3Rh2N, too. In ReT (T = transition metal) alloys [20–23], whose DOS is dominated by the Re 5d orbitals (with negligible contributions from the T metal orbitals), even a robust increase in SOC—from 3d Ti to 5d Ta—is shown to not significantly affect the superconducting properties. Conversely, similarly to the Li2(Pd, Pt)3B case, SOC effects are expected to be more important in Mo3Rh2N. Therefore, a comparative microscopic study of Mo3Rh2N vs Mo3Al2C is very instructive for understanding the (A)SOC...
effects on the superconducting properties of NCSCs. Another goal of this study was the search for a possible TRS breaking in the superconducting state of Mo$_3$Rh$_2$N.

In this Rapid Communication, we report on the systematic magnetization, thermodynamic, and $\mu$SR investigations of the recently discovered Mo$_3$Rh$_2$N NCSC. In particular, zero-(ZF) and transverse-field (TF) $\mu$SR measurements allowed us to study the microscopic superconducting properties and to search for a possible TRS breaking below $T_c$ in Mo$_3$Rh$_2$N.

**Experimental details.** Polycrystalline Mo$_3$Rh$_2$N samples were synthesized by solid-state reaction and reductive nitridation methods, whose details are reported elsewhere [17]. The room-temperature x-ray powder diffraction confirmed the $\beta$-Mn-type crystal structure, with no detectable extra phases [17]. The magnetization and heat-capacity measurements were performed on a 7-T Quantum Design magnetic property measurement system (MPMS) and a 9-T physical property measurement system (PPMS). The bulk $\mu$SR measurements were carried out using the general-purpose surface-muon (GPS) and the low-temperature facility (LTF) instruments of the πM3 beamline at the Swiss muon source of Paul Scherrer Institut, Villigen, Switzerland. For measurements on LTF, the samples were mounted on a silver plate using diluted GE varnish. The $\mu$SR data were analyzed by means of the MUSRFIT software package [24].

**Characterizing bulk superconductivity.** The magnetic susceptibility of Mo$_3$Rh$_2$N was measured using both field-cooled (FC) and zero-field-cooled (ZFC) protocols in an applied field of 1 mT. As shown in Fig. 1(a), the ZFC-susceptibility indicates bulk superconductivity below $T_c = 4.6$ K in Mo$_3$Rh$_2$N, consistent with the previously reported value [17]. The lower critical field $\mu_0H_{c1}$ was determined from the field-dependent magnetization $M(H)$, measured at various temperatures below $T_c$. The estimated $\mu_0H_{c1}(T)$ values are shown in the inset of Fig. 1(a). The solid line represents a fit to $\mu_0H_{c1}(T) = \mu_0H_{c1}(0)[1 - (T/T_c)^2]$ and yields a lower critical field $\mu_0H_{c1}(0) = 18(1)$ mT. The bulk superconductivity of Mo$_3$Rh$_2$N was further confirmed by heat-capacity measurements [see Fig. 1(b)]. The specific heat, too, exhibits a sharp transition at $T_c$, which shifts towards lower temperature upon increasing the magnetic field. The sharp transitions ($\Delta T \sim 0.3$ K) in both the specific-heat and magnetic-susceptibility data indicate a good sample quality. The derived $T_c$ values versus the applied field are summarized in the inset of Fig. 1(b), from which the upper critical field $\mu_0H_{c2}$ was determined following the Werthamer-Helfand-Hohenberg (WHH) model [25]. The solid line in the inset of Fig. 1(b) represents a fit to the WHH model, without considering spin-orbit scattering, and gives $\mu_0H_{c2}(0) = 7.32(1)$ T, consistent with the previously reported value [17].

**Transverse-field $\mu$SR.** To explore the microscopic superconducting properties of Mo$_3$Rh$_2$N, TF-$\mu$SR measurements were performed down to 0.02 K. In order to track the additional field-distribution broadening due to the flux-line lattice (FLL) in the mixed superconducting state, a magnetic field of 30 mT [i.e., larger than the lower critical field $\mu_0H_{c1}(0)$] was applied at temperatures above $T_c$. The TF-$\mu$SR time spectra were collected at various temperatures up to $T_c$, following a field-cooling protocol. Figure 2(a) shows two representative TF-$\mu$SR spectra collected above (6.4 K) and below $T_c$, respectively, with the latter not undergoing any depolarization. The faster, FLL-induced decay in the superconducting state is clearly seen in the second case. The time evolution of the $\mu$SR asymmetry is modeled by

$$A_{TF} = A_s \cos(\gamma \mu_B S_t + \phi) e^{-\sigma^2 t^2/2} + A_{bg} \cos(\gamma \mu_B B_{bg} t + \phi).$$

(1)

Here, $A_s$ 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. The $A_s/A_{TF}$ ratios were determined from the long-time tail of TF-$\mu$SR spectra at the base temperature [see Fig. 2(a)] [26], and fixed to 0.88 (GPS) and 0.90 (LTF) for all the temperatures. $B_s$ and $B_{bg}$ are the local fields sensed by implanted muons in the sample and sample holder, $\gamma = 2\pi \times 135.53$ MHz/T is the muon gyromagnetic ratio, $\phi$ is the shared initial phase, and $\sigma$ is a Gaussian relaxation rate. The Gaussian nature of relaxation is clearly evinced from the fast-Fourier-transform (FFT) spectra shown in Figs. 2(b) and 2(c). In the mixed superconducting state, the faster decay of muon-spin polarization reflects the inhomogeneous field distribution due to the FLL, which causes the additional distribution broadening in the mixed state [see Fig. 2(c)]. In the superconducting state, the measured Gaussian relaxation rate includes contributions from both a temperature-independent relaxation due to nuclear moments ($\sigma_n$) and the FLL ($\sigma_q$). The FLL-related relaxation can be extracted by subtracting the shared initial phase, and

![FIG. 1.](image-url)
FIG. 2. (a) The Mo$_3$Rh$_2$N TF-$\mu$SR time spectra, collected at 0.02 and 6.4 K in an applied field of 30 mT, show very different relaxation rates. Fourier transforms of the above time spectra at (b) 6.4 K and (c) 0.02 K. The solid lines are fits to Eq. (1) using a single Gaussian relaxation; The dashed lines indicate the applied magnetic field. Note the clear diamagnetic shift below $T_c$ in (c).

The nuclear contribution according to $\sigma_{sc} = \sqrt{\sigma^2 - \sigma_n^2}$. The derived Gaussian relaxation rate and the diamagnetic field shift as a function of temperature are summarized in Fig. 3. The relaxation rate, shown in Fig. 3(a), is small and independent of temperature for $T > T_c$, but it starts to increase below $T_c$, indicating the onset of FLL and an increase in superfluid density. Concomitantly, a diamagnetic field shift appears below $T_c$ [see Fig. 3(b)].

Since $\sigma_{sc}$ is directly related to the magnetic penetration depth and the superfluid density ($\sigma_{sc} \propto 1/\lambda^2$), the superconducting gap value and its symmetry can be determined from the measured $\sigma_{sc}(T)$. For small applied magnetic fields ($H_{appl}/H_{c2} \sim 0.004 \ll 1$), the magnetic penetration depth $\lambda$ can be calculated from [27,28]

$$\frac{\sigma_{sc}^2(T)}{\gamma^2} = 0.00371 \frac{\Phi_0^2}{\lambda^2(T)}.$$  \hspace{1cm} (2)

Figure 4 shows the inverse square of the magnetic penetration depth (proportional to the superfluid density) as a function of temperature for Mo$_3$Rh$_2$N. To gain insight into the SC pairing symmetry in Mo$_3$Rh$_2$N, its temperature-dependent superfluid density $\rho_{sc}(T)$ was further analyzed by using different models, generally described by

$$\rho_{sc}(T) = 1 + 2 \left\langle \int_0^\infty \frac{E}{E^2 - \Delta_k^2} \frac{\partial f}{\partial E} dE \right\rangle_{FS},$$  \hspace{1cm} (3)

where $\Delta_k$ is an angle-dependent gap function, $f = (1 + e^{E/k_B T})^{-1}$ is the Fermi function, and \langle \rangle$_{FS}$ represents an average over the Fermi surface [29]. The gap function can be written as $\Delta_k(T) = \Delta(T) g_k$, where $\Delta$ is the maximum gap value and $g_k$ is the angular dependence of the gap, equal

FIG. 3. Temperature dependence of (a) the muon-spin relaxation rate $\sigma(T)$ and (b) diamagnetic field shift $\Delta B(T)$ for Mo$_3$Rh$_2$N measured in an applied field of 30 mT. Here, $\Delta B = B_i - B_{bg}$, where $B_{bg}$ is the same as the applied magnetic field.

FIG. 4. Superfluid density vs temperature, as determined from TF-$\mu$SR measurements. The different lines represent fits to various models, including $s$-, $d$-, and $p$-wave pairing (see text for details).
to 1, \cos 2\psi, and \sin \theta for an s-, d-, and p-wave model, respectively. Here, \psi and \theta are azimuthal angles. The temperature dependence of the gap is assumed to follow \( \Delta(T) = \Delta_0 \tanh(1.82[1.018(T_c/T - 1)^{0.51}] \) [29], where \( \Delta_0 \), the gap value at zero temperature, is the only adjustable parameter. Note that the function \( \Delta(T) \) is practically independent of the used models.

Three different models, including s-, d-, and p-wave, were used to describe the temperature-dependent superfluid density \( \lambda^{-2}(T) \). By fixing the zero-temperature magnetic penetration depth \( \lambda_0 = 586(3) \text{ nm} \), the estimated gap values for the s- and p-wave model are 0.76(1) and 1.07(1) meV, respectively, while for the d-wave model, the estimated \( \lambda_0 \) and gap value are 536(3) \text{ nm} \) and 1.11(1) meV. As can be seen in Fig. 4, the temperature dependence of the superfluid density is clearly consistent with a single fully gapped s-wave model. In case of d- or p-wave models, a poor agreement with the measured \( \lambda^{-2} \) values is found, especially at low temperature. The s-wave nature of SC is further confirmed by the temperature-independent behavior of \( \lambda^{-2}(T) \) for \( T < 1/3T_c \), which strongly suggests a nodeless superconductivity in Mo3Rh2N. Such a conclusion is supported also by low-\( T \) specific-heat data [17].

Unlike the clean-limit case [see Eq. (3)], in the dirty limit the coherence length \( \xi \) is much larger than the electronic mean free path \( \ell_e \). In this case, in the BCS approximation, the temperature dependence of the superfluid density is given by [29]

\[
\rho_{sc}(T) = \frac{\Delta(T)}{\Delta_0} \tanh \left( \frac{\Delta(T)}{2k_B T} \right). \tag{4}
\]

Following the above equation, the estimated gap value is 0.68(1) meV, slightly smaller than the clean-limit value, yet still in excellent agreement with the gap values extracted from low-\( T \) specific-heat (0.67 meV) and Andreev-reflection spectroscopy data (0.59 meV) [17]. Such a “dirty” nature of SC might reflect the large electrical resistivity \( (\rho_0 = 0.48 \text{ m\Omega cm}) \) and the small residual resistivity ratio (RRR \( \sim 1 \) of Mo3Rh2N. The 2/\( k_B T \) ratios of about 3.46 (dirty limit) and 3.84 (clean limit) are both comparable to 3.53, the ideal value expected for a weakly coupled BCS superconductor.

Zero-field \( \mu \)SR. We performed also ZF-\( \mu \)SR measurements, in order to search for a possible TRS breaking in the superconducting state of Mo3Rh2N. The large muon gyromagnetic ratio, combined with the availability of 100% spin-polarized muon beams, make ZF-\( \mu \)SR a very sensitive probe for detecting small spontaneous magnetic fields. This technique has been successfully used to detect the TRS breaking in the superconducting states of different types of materials [20,22,30–33]. Normally, in the absence of external fields, the onset of SC does not imply changes in the ZF muon-spin relaxation rate. However, if the TRS is broken, the onset of tiny spontaneous currents gives rise to associated (weak) magnetic fields, readily detected by ZF-\( \mu \)SR as an increase in muon-spin relaxation rate. Given the tiny size of such effects, we measured the ZF-\( \mu \)SR spectra with high statistics in both the normal and the superconducting phases. Representative ZF-\( \mu \)SR spectra collected above (8 K) and below (1.5 K) \( T_c \) for Mo3Rh2N are shown in Fig. 5. For nonmagnetic materials, in the absence of applied fields, the relaxation is mainly determined by the randomly oriented nuclear moments, which can be described by a Gaussian Kubo-Toyabe relaxation function \( G_{KT} = \left[ \frac{1}{2} + \frac{1}{2}(1 - \sigma^{-2}) \right] e^{-\Delta^2/2\sigma^2} \) [34,35]

\[
A_{ZF} = A_s G_{KT} e^{-\Delta^2/\sigma^2} + A_{bg}. \tag{5}
\]

Here, \( A_s \) and \( A_{bg} \) are the same as in the TF-\( \mu \)SR case [see Eq. (1)]. The resulting fit parameters are summarized in Table I. The weak Gaussian and Lorentzian relaxation rates reflect the small value of Mo3Rh2N nuclear moments. The relaxations show very similar values in both the normal and the superconducting phase, as demonstrated by a lack of visible differences in the ZF-\( \mu \)SR spectra above and below \( T_c \). This lack of evidence for an additional \( \mu \)SR relaxation below \( T_c \) implies that TRS is preserved in the superconducting state of Mo3Rh2N. Since TRS is preserved also in the Mo3Al2C sister compound, this explains the many common features shared by these two \( \beta \)-Mn-type NCSCs [16].

**Discussion.** Since the admixture of spin-singlet and spin-triplet pairing depends on the strength of ASOC [4], the latter plays an important role in determining the superconducting properties of NCSCs. An enhanced ASOC can turn a fully gapped \( s \)-wave superconductor into a nodal superconductor, with typical features of spin-triplet pairing, as exemplified by the Li2(Pd, Pt)3B case. However, a larger SOC is not necessarily the only requirement for a larger ASOC and an enhanced band splitting \( E_{ASOC} \), since the latter two depend also on the

**TABLE I.** Fit parameters extracted from ZF-\( \mu \)SR data for Mo3Rh2N (collected above and below \( T_c \)) by using the Eq. (5) model.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>1.5 K</th>
<th>8 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_s )</td>
<td>0.24814(83)</td>
<td>0.24833(73)</td>
</tr>
<tr>
<td>( \sigma ) (( \mu )s(^{-1}))</td>
<td>0.0366(69)</td>
<td>0.0379(58)</td>
</tr>
<tr>
<td>( \Lambda ) (( \mu )s(^{-1}))</td>
<td>0.0069(32)</td>
<td>0.0047(28)</td>
</tr>
<tr>
<td>( A_{bg} )</td>
<td>0.01985(83)</td>
<td>0.01987(73)</td>
</tr>
</tbody>
</table>
specific crystal and electronic structures. The 4d-Rh, 4d-Ru, and 5d-Ir are heavy SOC metals, but their ASOC-related band splittings $E_{\text{ASOC}}$ are relatively small in some materials. For example, the expected $E_{\text{ASOC}}$ values for Ce(Rh, Ir)Si$_2$, LaRhSi$_3$, Rh$_3$Ga$_9$, and Ru$_3$B$_3$ are less than 20 meV (i.e., ten times smaller than in CePt$_3$Si or Li$_2$Pt$_3$B) [3]. Therefore, their pairing states remain in the spin-singlet channel and all of them behave as fully gapped superconductors. In $\beta$-Mn-type materials, such as Mo$_3$Rh$_2$N, the replacement of a light metal such as Al by the heavy Rh does indeed increase the SOC, yet the $E_{\text{ASOC}}$ still remains weak. Hence, the superconducting pairing is of spin-singlet type, in good agreement with both TF- and ZF-$\mu$SR results. Further band-structure calculations, which explicitly take into account the SOC effects, are needed to clarify this behavior.

Summary. We performed comparative $\mu$SR experiments to study the superconducting properties of NCSC Mo$_3$Rh$_2$N. Bulk superconductivity with $T_c = 4.6$ K was characterized by magnetization and heat-capacity measurements. The temperature variation of the superfluid density reveals nodeless superconductivity in Mo$_3$Rh$_2$N, which is well described by an isotropic $s$-wave model and is consistent with a spin-singlet pairing. The lack of spontaneous magnetic fields below $T_c$ indicates that time-reversal symmetry is preserved in the superconducting state of Mo$_3$Rh$_2$N.

Acknowledgments. This work was supported by the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung, SNF (Grants No. 200021-169455 and No. 206021-139082) and the National Natural Science Foundation of China (Grant No. 11504378).


[26] Due to the complete decay of the sample-related asymmetry beyond 7 $\mu$s, the residual signal is due to the background only.


