Magnetically-textured superconductivity in elemental Rhenium

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Recent μSR measurements revealed remarkable signatures of spontaneous magnetism coexisting with superconductivity in elemental rhenium. Thus pure rhenium could be the first elemental crystal where unconventional superconductivity is realized in nature. Here we provide a quantitative theory that uncovers the nature of the superconducting instability by incorporating every details of the electronic structure together with spin-orbit coupling and multi-orbital physics. We show that conventional s-wave superconductivity combined with strong spin-orbit coupling is inducing even-parity odd-orbital spin triplet Cooper pairs, and in presence of a screw axis Cooper pairs' migration between the induced equal-spin triplet component leads to an exotic magnetic state with atomic-scale texture. Our first-principles based model contains two phenomenological parameters that characterizes the pairing interaction fixed by the experimental value of the superconducting transition temperature and the slope of the specific heat, and allows quantitative prediction of the magnetic structure.

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INTRODUCTION

Superconductivity is the state of matter in which the electronic wave function spontaneously locks into a value with a definite complex phase. In some unconventional superconductors this form of symmetry breaking is simultaneous with additional breaking of time-reversal symmetry (TRS) indicating that the superconducting state is intrinsically magnetic [1]. Such systems are expected to have important applications in spintronics [2] and topological quantum computing [3] however this is hindered by the lack of a general theory of unconventional superconductivity [4, 5] which is normally associated with strong electron correlations or fluctuations of competing ordered phases. Recently, however, TRS breaking has been discovered by μSR measurements in seemingly ordinary superconductors where such exotic physics are not at play [6], including the chemical element Rhenium [7]. Detailed density-functional theory calculations confirm that the effect in these systems is intrinsic and not the result of the muon acting as a perturbation [8].

In Ref. [9] it was suggested that the electron-phonon and Coulomb interactions could lead to a multidimensional order parameter which breaks TRS. However, this assumes that the Fermi surface forms pockets around several points of high symmetry. Here we show that even without these conditions TRS breaking can occur simultaneously with the superconducting instability in electron-phonon driven superconductors which features strong spin-orbit coupling (SOC) and non-symmorphic crystal structure. One main difficulty of theories about unconventional superconductivity is that they rely on simplified models providing only a qualitative description of the phenomenon (in many cases even the qualitative understanding is problematic based on these models). However, a quantitative comparison to experimental data is needed to provide evidence for suggested pairing mechanisms. In this work we quantitatively prove that TRS breaking in elemental Rhenium crystals is due to a form of mixed singlet-triplet pairing that has an atomic-scale magnetic texture. Rather than assuming an unconventional pairing interaction from the outset, we couple a conventional pairing model with an *ab initio* description of the system's magnetism and electronic structure which is essential for quantitative predictions. We find that a triplet pairing component emerges spontaneously, without further symmetry breaking. When an additional pairing term operating in this channel is added in order to make our theory self-consistent a phase with broken time-reversal symmetry emerges. Through computer experiments we identify the non-symmorphic crystal structure as the key ingredient of this exotic new state. Our approach represents a significant departure from previous attempts at understanding symmetry-breaking in unconventional superconductors, yet it describes experimental data quantitatively with only two adjustable parameters, showing that unconventional superconductivity can be more ubiquitous than hitherto assumed.

KEY QUANTITIES OF SUPERCONDUCTING INSTABILITIES

The key physical quantity in all known superconductors is the spin-dependent anomalous density $\chi^{\alpha\beta}(\mathbf{x},\mathbf{y}) = \left\langle \Psi^{\alpha}(\mathbf{x})\Psi^{\beta}(\mathbf{y})\right\rangle$. Here α, β are spin indices ($\uparrow\downarrow$) and $\Psi^{\alpha}(\mathbf{x})$ is the annihilation field operator for an electron with spin α at $\mathbf{x}$. χ plays the role of an order parameter, that is, a quantity that becomes non-zero continuously when entering the ordered (superconducting) phase. Since χ represents pairing between two fermions it has to be antisymmetric with respect to the exchange of all the particle labels. It is common to use the Balian-Werthamer parametrisation $\chi = \sum_{j=S,T_x,T_y,T_z} i\chi^j \hat{\sigma}_j \sigma\sigma_y$ where $\hat{\sigma}_S, \hat{\sigma}_{T_x}, \hat{\sigma}_{T_y}, \hat{\sigma}_{T_z}$ represent, respectively, the 2×2 identity matrix and the σ_x, σ_y, and σ_z Pauli matrices. The singlet component of the anomalous density χ^S and the three triplet components $(\chi^{T_x}, \chi^{T_y}, \chi^{T_z})$ are antisymmetric and symmetric with respect to the exchange of the spin labels and behave as a scalar and a vector under spin rotations, respectively. More detailed symmetry classification of the order parameter χ can be found in Supplement II where the spatial behaviour of $\chi(\mathbf{x},\mathbf{y})$ is further divided into parity, orbitals and sub-lattices.

In mean field descriptions the anomalous density is explained by the spontaneous emergence of a pairing potential $\left(d^S, d^{T_x}, d^{T_y}, d^{T_z}\right)$ obeying a self-consistency equation

$$d^j(\mathbf{x},\mathbf{y}) = \sum_{\mathbf{x}',\mathbf{y}',j'} \Lambda^{j,j'}\left(\mathbf{x},\mathbf{y};\mathbf{x}',\mathbf{y}'\right)\chi^{j'}\left(\mathbf{x}',\mathbf{y}'\right) \tag{1}$$

where the kernel $\Lambda^{j,j'}\left(\mathbf{x},\mathbf{y};\mathbf{x}',\mathbf{y}'\right)$ describes pairing interactions (with j, j' denoting the spin channels according to the Balian-Werthamer parametrisation).

If the pairing potential is non-trivially complex then the superconducting state breaks TRS. This has been discovered in many superconductors [7, 10–32] chiefly using muon-spin relaxation (μSR), confirmed in some cases by SQUID magnetometry and/or the optical Kerr effect. Due to the second-order nature of the superconducting phase transition, just below T_c the pairing potential must be a linear superposition of basis functions of one of the irreducible representations (irreps) of the crystal space group [33]. Since the identity irrep is always one-dimensional, and therefore cannot lead to a non-trivially complex order parameter, it follows that a pairing potential with the full symmetry of the crystal lattice cannot break TRS. In this picture, TRS breaking at T_c can only be due to a pairing interaction kernel $\Lambda^{j,j'}\left(\mathbf{x},\mathbf{y};\mathbf{x}',\mathbf{y}'\right)$ favouring a low-symmetry (unconventional) pairing instability or to the fine-tuning of an independent, magnetic instability to coincide with T_c (as special point in the phase diagram of ferromagnetic superconductors [34]). The theory of broken TRS that we present here falls outside both scenarios: on the one hand, our pairing kernel is conventional (i.e. it induces an anomalous density that respects the symmetry of the crystal); on the other hand, the magnetic transition that we find is inextricably linked to the superconductivity - specifically, it relies on a symmetry-preserving, but triplet component of the pairing potential.

QUANTITATIVE THEORY OF TRS BREAKING BASED ON FIRST-PRINCIPLES

In the last few years there is a rising awareness about the internal electronic degrees of freedom like orbitals and sub-lattices in the theory of superconductivity [35–52]: the pairing states depend on these internal degrees of freedom and may result in interesting phenomena like TRS breaking and Bogoliubov surfaces [43, 44]. To describe the superconductivity of Re in a way that captures accurately the effects of multiple orbitals and the crystal structure we use the density functional theory of superconductors [53] extended with relativistic effects [54, 55]. In this theory the anomalous density χ is treated on an equal footing with the electron density ρ and magnetisation $\mathbf{m}$. The theory features three potentials $d_{\text{eff}}(\mathbf{x},\mathbf{y})$, $V_{\text{eff}}(\mathbf{x})$, $\mathbf{B}_{\text{eff}}(\mathbf{x})$ coupling, respectively, to each of these densities. In principle all three potentials can be determined exactly through variation of an exchange-correlation free-energy functional $\Omega_{xc}[\rho, \mathbf{m}, \chi]$. In practice, the functional is not known and approximations have to be made. In our calculations we determine $V_{\text{eff}}(\mathbf{x})$ and $\mathbf{B}_{\text{eff}}(\mathbf{x})$ from first principles within the local spin-density approximation (LSDA). This is expected to yield an accurate, *ab initio* description of the normal-state magnetic and electronic properties together with spin-orbit coupling. These details of the normal state electronic structure can be found in Supplement I. These calculations reveal the importance of spin-orbit coupling and the complex structure of the Fermi surface with complex orbital character involving all the $5d$ orbitals.

To determine the pairing potential $d_{\text{eff}}(\mathbf{x},\mathbf{y})$ we adopt a generic self-consistency equation of the type (1) and make a physically-motivated choice for the interaction kernel. For elemental rhenium the symmetry analysis which could pin down the possible structures of the order parameter is complicated by the non-symmorphic structure [7]. Nevertheless in view of the BCS-like properties reported for the superconducting state of Rhenium [56] a reasonable starting point is a local, on-site, intra-orbital pairing interaction in the spin singlet channel described by a single adjustable parameter Λ giving the strength of the pairing interaction (for details of how this interaction is implemented see Supplemental Material IV). This can mimic a pairing mechanism caused by electron-phonon coupling accurately [57, 58]. The parameter Λ is fixed by the known value of the superconducting critical temperature, $T_{\text{c}} = 1.697 \pm 0.006\text{K}$ [59] giving $\Lambda = 0.67$ eV.

The theory can then be used to predict observable properties. Our treatment is fully relativistic and constrained by the known crystal structure of Re (see Supplemental Material IV).

RESULTS AND DISCUSSION

A comparison of the temperature-dependence of the electronic specific heat in the superconducting state, C_S, to experimental data is shown in Fig. 1. The calculation overestimates the specific heat jump at T_c and the rate at which C_S is suppressed as we lower the temperature. Moreover, unsurprisingly, it does not predict broken TRS. On the other hand the calculation predicts a complex anomalous density with two components: a singlet component with on-site, intra-orbital pairing as one would expect to emerge from our singlet pairing interaction and an additional, triplet component acting between electrons with equal spins that is also on-site but inter-orbital. This triplet component appears together with the singlet component at T_c and does not break any additional symmetries (in other words, our Ginzburg-Landau order parameter remains one-dimensional; the details of the superconducting order parameter structure are given in Supplement III). The singlet-triplet mixing is induced by spin-orbit coupling, similar to the triplet admixture thought to occur in a number of noncentrosymmetric superconductors [60]. While in a single-band picture such admixtures are only possible when the crystal lacks inversion symmetry [61] in a multi-orbital system the possibility exists for centrosymmetric systems as well. Here *the SOC leads to orbitally antisymmetric, spin-off diagonal terms of the Hamiltonian which allows the emergence of interorbital (orbitally antisymmetric) triplet pairings* (see Supplement II for a detailed discussion).

The presence of this additional component in the anomalous pairing density implies that an additional term needs to be added to our interaction kernel in order to make the theory self-consistent. We thus introduce an additional parameter Λ_{EOT} setting the strength of an on-site, inter-orbital, triplet component of the pairing interaction (the notation emphasises that the second component of the order parameter is Even under parity, Odd under orbital exchange and Triplet as regards spin exchange, see Supplement II). Given the presence of a triplet pairing component of the anomalous density with the same structure even in the absence of the triplet interaction,we do not need to assume an interaction of this term arises from a unconventional pairing mechanism. The interaction may result from the combination of a conventional, phonon-mediated mechanism with the same SOC effects that lead to the triplet anomalous density when it is not present. We note that Hund's coupling can also induce EOT states [62, 63] but elemental Rhenium is not considered to be a Hund's metal. As shown in Fig. 1 the temperature dependence of C_S depends sensitively on the value of Λ_{EOT} and a very good fit to experiment is obtained using $\Lambda = 0.61$ eV, $\Lambda_{\mathrm{EOT}} = 0.38$eV.

Remarkably, for the value of Λ_{EOT} that captures the correct behaviour of C_S we also find broken TRS. Specifically, a magnetic moment appears on each of the two Re sites within the unit cell at T_c. These magnetic moments grow continuously as the temperature is lowered, reaching a saturated value of $0.01\mu_B$ per Re atom in the ground state. However, the magnetic moments on both Re atoms point in opposite directions, so the total magnetic moment within the unit cell averages to zero at all temperatures. This is different from both ferromagnetism and anti-ferromagnetism. Note in particular that unlike an antiferromagnet in the present state translational symmetry is not broken. Instead, this magnetic state breaks both the internal screw-axis symmetry of the unit cell and time-reversal symmetry without breaking the combination of screw axis and time-reversal. We mention that there is a similar effect in the normal state of non-magnetic crystals with inversion symmetry: SOC can induce momentum dependent spin polarization which leads to spin-orbit coupled Bloch wave functions having different spin polarisations on different atomic orbitals [64, 65]. In Re, however, the magnetic texture appears only in the superconducting state, as we discuss below.

The maximum internal magnetic field resulting from this magnetic moment of the rhenium atoms can be estimated by $B_{int}^{max} = \mu_0\mu_s/(4\pi abc) \approx 0.06$ mT which is comparable to the value measured experimentally by muons, 0.02 mT [7] (we note as a local probe the muons will typically see a lower value than the maximum estimated). However, due to the zero net magnetic moment we predict that an NMR experiment which could measure the magnetism of the whole unit cell would not detect TRS breaking in the superconducting phase of Re.

A microscopic insight into how this new state comes about can be gained from examination of the zero-temperature quasi-particle density of states (DOS), also shown in Fig. 1. The DOS has multiple superconducting gaps, which is consistent with thermodynamic measurements [56, 66]. Two gaps can be clearly distinguished with the values of 0.25 eV and 0.31 eV.[67] However, when resolved by atomic site and spin label we see that these multiple gaps have their origin not in the band structure, but in the magnetic nature of the superconducting state. Specifically, they are due to different gaps in the spin-up and spin-down channels on a given site. Thus, the net magnetic moment on each site can be understood as a result of Cooper pair migration, proposed by Miyake for Sr_2RuO_4 [68] and thought to occur in $LaNiC_2$ and $LaNiGa_2$ [17, 32, 38, 69]: electrons flip their spin to maximise a free-energy advantage awarded to equal-spin Cooper pairs, resulting in unequal Cooper pairing strength in the spin-up and spin-down channels.

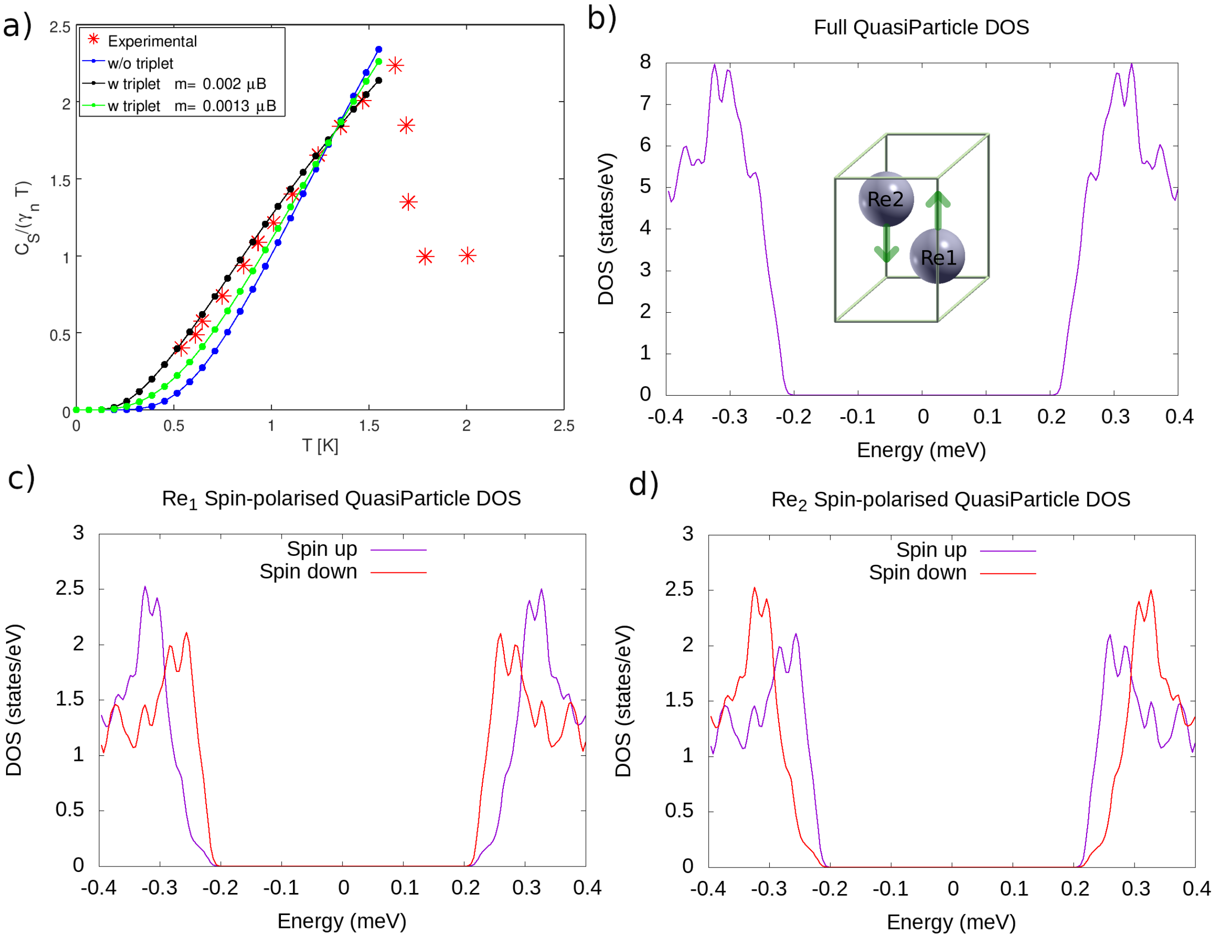

Figure 1. (a) Temperature-dependence of the specific heat in the superconducting state C_S normalised its normal-state value. Red asterisks: experimental data from Ref. [56]. Blue line: calculation with the purely singlet pairing interaction of strength $\Lambda = 0.67$ eV leading to no magnetic moment. Black line: calculation with singlet and symmetry-preserving triplet pairing strengths $\Lambda = 0.61$ eV, $\Lambda_{\mathrm{EOT}} = 0.38$eV leading to a low-temperature magnetic moment $m = 0.002\mu_B$. Green line: the same as the black line, but with Λ_{EOT} decreased by 24%, as indicated, corresponding to ground-state magnetic moment of $0.0013\mu_B$. To normalise the experimental data the specific heat was divided by $\gamma_n T$ with the Sommerfeld coefficient γ_n chosen to fit the normal-state data at $T = 2$K. To normalise the calculated values we divided them by the same quantity obtained with the pairing potential artificially turned to zero (see Supplement IV). (b-d) Density of states in the superconducting state of rhenium: the (b) figure shows the full quasi-particle DOS. The (c) and (d) figures show the spin-resolved DOS on the Re1 site (c) and the Re2 site (d). The inset to panel (b) shows the unit cell with the direction of the obtained magnetic moment on each atom indicated by the green arrows. Note that the two magnetic moments are anti-parallel so the total magnetic moment of the unit cell is zero however translational symmetry is not broken. Hence, this intra-cell magnetic texture is qualitatively distinct from both ferromagnetism and antiferromagnetism.

However, as shown in the figure in the case of Re the effect is reversed between sites 1 and 2, leading to no net magnetisation. We note also that in the present case the pairing takes place principally in the singlet channel, and does not by itself (without migration) break any additional symmetries, while in Refs. [17, 32, 68, 69] the instability is purely triplet and breaks SO(3) symmetry spontaneously, even without Cooper pair migration. Our findings therefore constitute to a strong generalisation of our understanding of this route to TRS breaking very considerably (we note in passing that pair migration itself can be regarded as a generalisation to Cooper pairs of the Stoner instability, which is the paradigmatic mechanism of TRS breaking for unpaired conduction electrons). The direct observation of such atomic-scale magnetic structures are possible with spin-sensitive scanning probe methods [70].

Further insight into the unusual superconducting state of Re can be gained by investigating the phase diagram of our theory as the parameter Λ_{EOT} is varied away from the experimentally-relevant value. This is shown in Fig. 2. The phase diagram shows three distinct thermodynamic phases: a normal state with TRS, a superconducting phase with TRS, and a second superconducting phase

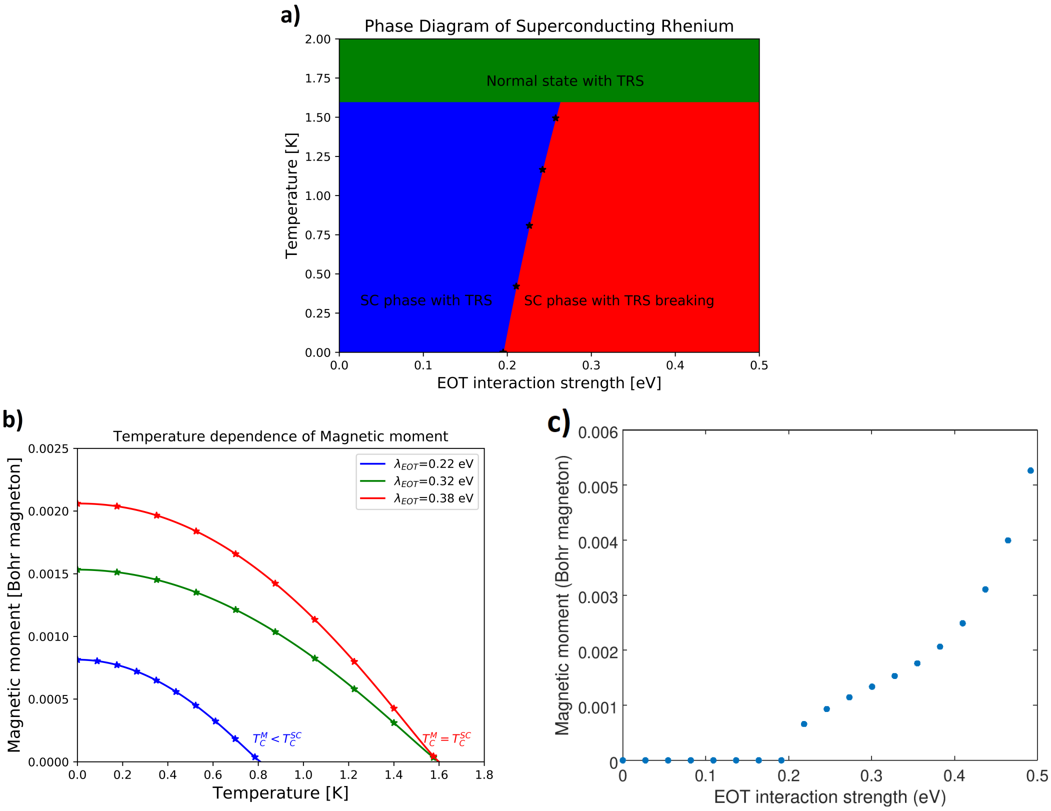

Figure 2. (a) Phase diagram of Re as a function of temperature T and the strength Λ_{EOT} of the triplet pairing interaction strength. See the main text for a description of the physics in each region. The bottom panels show the dependence of the Re-site magnetic moment (c) on Λ_{EOT} at $T = 0$ and (b) the dependence of the same quantity on T for three fixed values of Λ_{EOT}, as indicated. In all the plots, the singlet pairing interaction strength Λ has been chosen so as to produce the correct normal-state critical temperature. The dashed line on the phase diagram marks the value of Λ_{EOT} for which the specific heat temperature dependence is also correctly captured (see Fig. 1).

where the Re sites have finite magnetic moments and which therefore breaks TRS. All the phase boundaries are of second-order which is consistent with all three states possessing different symmetries. The three boundaries meet at a tri-critical point. We note that there is never any magnetism in the normal state, which shows that the broken TRS is inherent to the superconductivity.

The second-order transition between two distinct superconducting phases in the phase diagram of Fig. 2 is a telltale signature of an unconventional superconducting state. We emphasize that the triplet component of the order parameter is finite on either side of that boundary. However, on the high-symmetry side this component is unitary and does not break any additional symmetries, while on the low-symmetry side it becomes non-unitary through Cooper pair migration. This is a generalisation of the coupling of nonunitary triplet pairing to magnetisation discussed in Ref. [17] in the context of LaNiGa$_2$, and that may also apply to the heavy-fermion material UTe$_2$ [71], which favours the nonunitary channel of a triplet instability. Our results imply that this mechanism can act through more general types of magnetic order parameter. Another crucial difference is that in the case of Re the unitary triplet pairing is induced by spin-orbit coupling and does not break any additional symmetries. More interestingly based on Fig. 2 one can also identify a region of Λ_{EOT} where the transition temperature related to broken TRS is smaller than the superconducting critical temperature.

In line with the above discussion, we may interpret the broken TRS phase as the result of a finite susceptibility to forming a magnetically-textured state that couples to the triplet component of the order parameter. Since broken TRS is not observed in a majority of superconductors, the question remains why Re is particularly susceptible to this type of magnetic order. Given that it involves the breaking of the screw-axis symmetry between the Re1 and Re2 sites, we hypothesise that the crucial ingredient is this non-symmorphic feature of the crystal structure. To test this hypothesis, we have performed two computational experiments where the crystal structure is artificially altered to reduce the effect of this symmetry and the magnetic moment on each Re atom in the ground state is obtained. The results are presented in

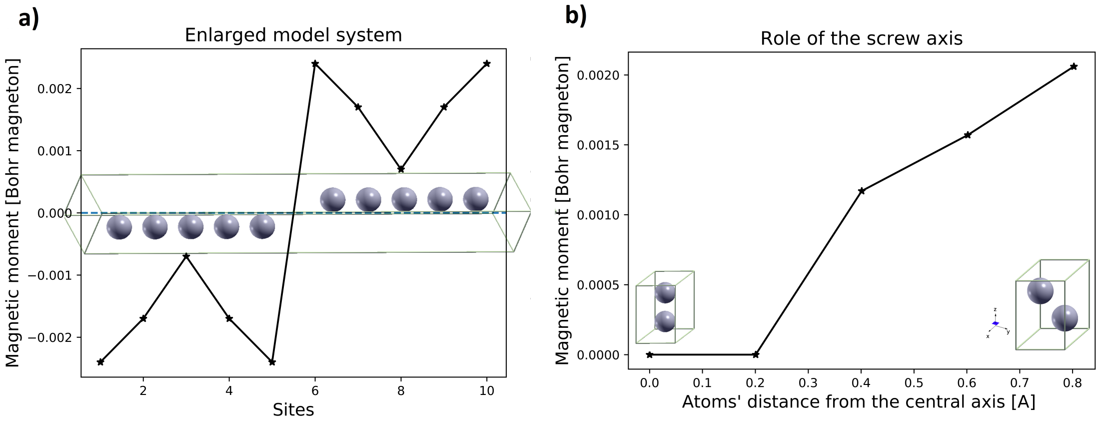

Figure 3. Effect of artificially distorted lattice structures. (a) Magnetic moments for the enlarged model system and (b) the primitive cell of the model system where the atoms' distance from the central axis is decreased step by step until the screw axis is removed.

Fig. 3. In the first computational experiment we enlarge the unit cell in the z-direction by creating five copies of each of the two Re atoms, placed at regular intervals in that direction (see figure). The result is equivalent to an infinite stack of 5-atom thick slabs of material where the screw-axis symmetry has been removed, but that symmetry still connects the top atom in one slab to the bottom atom on the next one. We find that the magnetic moment persists at the interface, but it is rapidly suppressed away from it. Moreover, all the moments within a slab point in the same direction, which switches at the interface. This suggests a deep analogy with the theory proposed by Aharata et al. [72] for twin boundaries in time-reversal symmetric non-centrosymmetric superconductors with singlet-triplet admixture, according to which the superconducting state breaks spontaneously the bulk time-reversal symmetry locally near the twin boundary. One can envisage the non-symmorphic structure of Re as an infinite stack of 1-atom thick twin boundaries. This connects the singlet-triplet mixing well known from non-centrosymmetric superconductors [60] to that observed here. In the second computational experiment, the atoms' distance d from the central z-axis is decreased continuously until the screw axis is removed (see figure). We find that the size of the magnetic moment decreases rapidly as d is reduced and the magnetic moment vanishes completely when it reaches a finite, critical value. This confirms the role of the screw axis in bringing about the broken TRS.

The tri-critical point at $\Lambda_{\mathrm{EOT}}^{\mathrm{crit.}} \approx 0.26$ eV is an interesting target for future investigations. This value of Λ_{EOT} is 31.6% smaller than the experimentally-relevant value for Re. On the basis of Fig. 3 (b) we speculate that high pressure measurements may split the two critical temperatures similarly to what was measured in the recent experiments of superconducting $\mathrm{Sr_2RuO_4}$ [73], offering another route to investigate the tri-critical point. We also mention that both theoretical studies [74] and Spin- and Angle-Resolved Photoemission Spectroscopy measurements [75] already suggested the coexistence of spin singlet and spin triplet Cooper pairs in case of $\mathrm{Sr_2RuO_4}$ (which has centrosymmetric crystal structure) which could be related to the observed Knight shift related to in-plane fields [76].

SUMMARY AND CONCLUSION

In summary a new TRS breaking mechanism was identified in s-wave superconductors with strong spin-orbit coupling and non-symmorphic (centrosymmetric) crystal structure. Our theory contradicts the idea that unconventional superconductivity is related to chemical complexity and it is considerably different from the non-unitary triplet pairing proposed earlier in $\mathrm{LaNiC_2}$ [69] and $\mathrm{LaNiGa_2}$ [17, 32] where the triplet pairing is inherently driven by an unconventional pairing mechanism and the superconducting ground state is ferromagnetic. However, in Rhenium we have shown that there is an admixed singlet-triplet pairing caused by the orbitally antisymmetric part of spin-orbit coupling on top of conventional phonon driven superconductivity and yields a nontrivial magnetic texture. This is very different also of typical admixed states in non-centrosymmetric superconductors where the triplet component does not lead to bulk TRS breaking. An ab-initio based quantitative description with two phenomenological parameters could fit the recently available experimental data for rhenium making it the first elemental crystal where signatures of unconventional superconductivity were identified both experimentally [7] and theoretically. In the broader context our results imply that superconductivity and magnetism can not be viewed simply as competing order parameters in case of electron-phonon driven s-wave superconductors. In fact, the internal structure of the pairing potential emerging from multiorbital physics has lead to a cooperative interplay between superconductivity and magnetism.

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