The interface between Sr$_2$RuO$_4$ and Ru-metal inclusion—Implications for its superconductivity

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Under various conditions of the growth process, when the presumably unconventional superconductor Sr$_2$RuO$_4$ (SRO) contains micro-inclusions of Ru metal, the superconducting critical temperature increases significantly. An STEM study shows a sharp interface geometry which allows crystals of SRO and of Ru-metal to grow side by side by forming a commensurate superlattice structure at the interface. In an attempt to shed light as to why this happens, we investigated the atomic structure and electronic properties of the interface between the oxide and the metal micro-inclusions using density functional theory (DFT) calculations. Our results support the observed structure indicating that it is energetically favored over other types of Ru-metal/SRO interfaces. We find that a $f_{3g}$-$e_g$ orbital mixing occurs at the interface with significantly enhanced magnetic moments. Based on our findings, we argue that an inclusion mediated interlayer coupling reduces phase fluctuations of the superconducting order parameter which could explain the observed enhancement of the superconducting critical temperature in SRO samples containing micro-inclusions.

I. INTRODUCTION

The superconducting state of Sr$_2$RuO$_4$ (SRO) has been intensively studied since its discovery in 1994. SRO is a layered perovskite oxide sharing the same structure as La$_2$CuO$_4$, one of the parent compounds of the cuprate superconductors, and it is believed to be a $p$-wave superconductor with odd spin-triplet pairing. A chiral orbital order parameter of the form $p_x + ip_y$ has been suggested by time-reversal symmetry breaking experiments. The role of strong ferromagnetic spin fluctuations in mediating superconductivity has been pointed out. Theoretical and experimental investigations which were carried out before 2002 have been reviewed. Quantum oscillation experiments indicate that the normal state can be understood as a two dimensional Fermi liquid.

The electronic properties have been studied by a number of methods which are summarized in Ref. 1, including the local density approximation (LDA) method and the generalized gradient approximation (GGA) method. Depending on the exchange correlation functional used, GGA predicts either a nonmagnetic state or an antiferromagnetic (AF) state with ferromagnetically ordered RuO$_2$ basal planes.

In more recent studies, superconductivity in bulk SRO is found to be enhanced under uniaxial (001), (100) and (110) strains where in the latter two cases strain-driven asymmetry of the lattice is believed to cause a change in symmetry of the superconducting order parameter. $T_c$ is also found to be enhanced due to dislocations, and in a system where there is an interface of W/Sr$_2$RuO$_4$ point contacts.

The unexpected enhancement of $T_c$ from 1.5 K to almost 3 K, when micro-sized ruthenium metal inclusions are embedded inside SRO in the eutectic system during crystal growth, is a very interesting and unexplained phenomenon. There is evidence that the “3-K” superconducting phase is unconventional with the presence of a hysteresis loop. In this “3-K” phase, the ruthenium micro-platelets are not uniquely oriented with respect to the SRO lattice. This, together with large diamagnetic shielding could suggest the existence of interface superconductivity at the Ru-SRO interface, residing primarily in SRO. Sigrist and Monien’s phenomenological analysis postulates a superconducting state with different symmetry and higher $T_c$ than in the bulk.

STEM images of a representative interface were presented in Ref. 27 and in the present paper with higher resolution as shown in Fig. 1. Here, we explore the atomic structure, stability and the electronic properties of this interface using density functional theory (DFT) calculations. We notice that this stable interface is perpendicular to the SRO bulk crystallographic $a$ axis and has alternating intact meandering Ru-O octahedra, which can be conceived as continuations of the bulk SRO Ru$_2$O$_7$ planes. Alternating pairs of Ru columns (which, as we show, are coordinated by oxygen atoms which are not visible in the STEM images) fill in the gaps created by the meandering interface at the same periodicity as the SRO unit cell along the crystallographic $c$ axis. These pair columns of Ru atoms have a coordination number different from that in the metal phase and that in the SRO phase. A nearly perfect hcp crystal of Ru metal grows from the next metal layer with a small lattice mismatch that eventually relaxes as one moves away from the interface and into the inclusion.

In the lowest energy interface the Ru-metal grows its
first layer commensurate with the SRO interface at a wavelength which nearly corresponds to eleven Ru metal atoms for every two periods of the SRO crystal along its own c axis. Therefore, the inclusions connect RuO$_2$ planes through a commensurate interface which is almost perfectly ordered at the atomic scale.

We show that this interface is stable against phase separation and it is more stable than other conceivable interfaces between SRO and Ru-metal. A spin polarized GGA calculation yields significant magnetic moments of the Ru atoms in the SRO phase near the interface. Our study establishes a clear picture of the stable Ru-Sr$_2$RuO$_4$ interface which is important in understanding the unconventional “3-K” phase.

We also argue that our findings, that the Ru inclusions form a nearly atomically perfect interface with the SRO crystal, imply the emergence of a significant interlayer coupling which could give rise to reduction of phase fluctuations of the superconducting order parameter characterizing the various RuO$_2$ planes. This is expected to lead to an enhancement of the superconducting critical temperature as observed in the SRO crystals with Ru inclusions.

The paper is structured as follows. In Sec. II, we present the computational details of our DFT calculations of the observed interface structure and stability consideration of various terminations. In Sec. III, we analyze STEM observations based on the DFT-based calculations and also discuss our detailed results obtained from these calculations. In Sec. IV, we discuss the possible causes of increased $T_c$ based on our findings. Last, in Sec. V, we highlight our conclusions and the implications of this work.

II. DFT STUDY OF THE INTERFACE STRUCTURE

The platelet inclusions are the result of excess Ru (more RuO$_2$ in the mixture than needed to make stoichiometric SRO) in the initial mixture. We will show by means of DFT calculations that the interface seen in our STEM images is low enough in energy to be preferable than macroscopic phase separation of SRO and Ru metal. In addition, we will show that other related interfaces are energetically higher than the one shown in Fig. 1.

Sr$_2$RuO$_4$ occurs in bulk in the body-centered tetragonal structure like the high temperature superconductor La$_2$CuO$_4$. Ru, the brightest atoms in the STEM images in the SRO phase, and the planar O(1) atoms form a two-dimensional square lattice with Ru-O bond length being 1.95 Å which is less than the sum of the ionic radii of Ru$^{4+}$ and O$^{2-}$, suggesting planar hybridization. The apical O(2) height above and below is larger at 2.06 Å.

![FIG. 1. (a) Scanning electron microscope image of a cleaved (001) Sr$_2$RuO$_4$ bulk crystal containing parallel Ru microplatelets (brighter contrasted short lines). (b) HAADF-STEM image of the Sr$_2$RuO$_4$/Ru interface at lower magnification showing an atomically straight and sharp superstructured interface, where the brighter region on the left is the Ru metallic inclusion and on the right is the Sr$_2$RuO$_4$ phase. The brightest spots are Ru followed by Sr. O atoms are too faint to be observed. There is no concentration gradient of SRO or Ru on either side of the interface. (inset) Close up view of the interface at higher magnification, where the atomic structure is clearly revealed. The HAADF-STEM images were taken with a probe of 0.078 nm and a convergence semi-angle of 21 mrad and inner collection angle of 78 mrad. Brighter-contrast atoms are Ru atoms while Sr atoms are less bright.](image)

A. Analysis of the observed interface

First, we notice in Fig. 1 and in Fig. 1 of Ref. 27 that the interface is perpendicular to the bulk [001] SRO direction and is terminated at alternating intact meandering Ru-O octahedra, which are continuations of the bulk SRO RuO$_2$ planes, and alternating pairs of Ru columns filling in the gaps created by the meandering interface. Notice that, as seen in Fig. 1, the Ru ions of the metallic interface, without any significant change of the unit-cell size, form an interface at a commensurate wavelength nearly twice that of the SRO unit-cell size in the [001] direction (corresponding to eleven unit cells of pure Ru...
crystal). The commensurate growth leaves a small lattice mismatch between the SRO layers near the interface and those deeper in the bulk. This causes a strain that grows with system size until it becomes energetically favorable to produce dislocations\textsuperscript{21} relieving the strain. As seen in the transmission electron microscopy (TEM) images in Ref. 21, the dislocations are complex structures which occur, for a sharp and flat interface, over a length scale longer than that visible in Fig. 1. These structures are beyond the scope of our present \textit{ab initio} calculations and we focus here on the microscopic length scale at which the interface is free of dislocations.

STEM image provides great information on the interface structure but leaves an ambiguity on any oxygen atom near the interface and the Ru atom positions in the SRO [010] direction which is perpendicular to the STEM field of view. This is the first item to address by means of our DFT calculations, the technical details of which are discussed later. By examining various possibilities, we find that in their optimum positions, the Ru pair columns bridge diagonal oxygen atoms of the terminating SRO layer. On one side of the interface these Ru pair columns form a similar type bond to oxygen atoms as the 1.95 Å Ru-O bond in the rutile phase of RuO\textsubscript{2} and on the other side they have an hcp Ru environment. This arrangement leaves the meandering SRO termination layer unchanged subject to ionic relaxations, and is consistent with the experimental image in Fig. 1. Therefore, we believe that this part of our DFT study complements the STEM image and we now have a complete picture of the structure of the interface.

B. Stability of the interface

The implementation of the observed structure by DFT calculation ideally requires at least eleven bulk unit cells of the hcp Ru metal phase commensurate with two conventional bulk unit cells of the SRO along the SRO [001] axis, and at least six bulk unit cells of the hcp Ru commensurate with four bulk units cells of the SRO along the SRO [010] direction. Such a supercell proved computationally unfeasible, particularly due to the large number of ruthenium atoms. Instead, to keep the supercell size reasonable, we used a supercell geometry with a stretched unit cell length of 13.52 Å along the SRO [001] direction and double the SRO bulk unit cell length in the SRO [010] direction.

In this reduced supercell containing 128 atoms, shown in Fig. 2, one conventional bulk SRO unit cell is commensurate with six bulk hcp Ru unit cells along SRO [001] and two bulk SRO unit cells are commensurate with three bulk metal unit cells in the SRO [010] direction. The atoms have been relaxed to their final positions. This geometry stretches the SRO c-axis by 5 % and compresses the a, b axes of the hcp Ru by 4 % each. The apical O(2) height is increased from 2.06 Å to 2.09 Å. In Fig. 3 we show the SRO b−c plane of the two layers of the SRO-Ru interface formed by the interface Ru pair columns and the terminating layer of the hcp metal. Even though we will use this smaller super-cell in our DFT implementation, by carrying out various types of optimization calculations it will become reasonably clear that the observed structure is indeed the most energetically favorable among various other plausible atomic configurations.

First, we find that the energy needed for breaking apart the interface of our reduced structure to create the two constituent slabs - SRO with [100] surfaces and Ru metal with [001] surfaces (Fig. 4) - to be 13.16 eV, a significant amount of energy.

Second, we compare the energy of our reduced structure to the energy of a similar supercell but with flat SRO [100] - Ru [001] interface (shown in Fig. 5) which we compute by bringing the SRO and Ru phases closer in small steps and relaxing the ions around their positions to find the minimum of the energy. We find that this supercell is higher in energy by 8.37 eV compared to our reduced meandering geometry in Fig. 2. Thus the meandering octahedra and the interface ruthenium columns are necessary to stabilize the interface. In both the above calculations, there are 128 atoms on either side of the equation and we account for the balance of atoms in the non-meandering structures by putting the extra Ru pair columns of the interface in a ruthenium bulk phase, which is the most stable ruthenium phase. To describe why the meandering Ru interface columns are necessary, consider the two interface layers (b−c plane of SRO) in Fig. 3. We note that the interface Ru columns form a rectangular planar lattice (which is commensurate with the same periodicity of our reduced interface geometry) adjacent to the triangular lattice of the terminating Ru
FIG. 3. (color-online) The SRO $b-c$ plane showing the two layers of the SRO-Ru interface, formed by the interface Ru pair columns and the terminating layer of the hcp metal. The unit cell lengths are slightly different from ideal bulk values (with details in the text). The triangular lattice of the Ru metal layer and the rectangular lattice of the interface Ru pairs are commensurate with 7.81 Å × 13.52 Å wavelengths in the SRO [010] and [001] directions respectively. The Ru columns are situated in the low energy valleys of the triangular lattice. The experimental wavelength is at least twice in each direction with an increased fraction of misalignment where some interface columns are located away from the hcp valleys, but the idea commensuration between a rectangular and a triangular lattice is preserved.

metal plane. Furthermore, the interface Ru pairs to a large extent are situated in potential valleys where the atoms of the next Ru hcp layer would have been in absence of an interface.

Third, having established the necessity of the meanders, we argue that the larger interface with eleven unit cells of Ru-metal in the SRO [001] direction and six Ru-metal unit cells in the SRO [010] direction is more stable than our computed reduced interface as follows.

The reduced geometry suffers from artificial planar compression of its Ru metal phase and uniaxial strain of its SRO phase but it accommodates the interface Ru pair columns in the grooves created by the terminating hcp Ru layer. By sliding the Ru metal phase across the interface in Fig. 2, we find that this is indeed an energy minimum. The larger experimentally observed periodicity breaks this symmetry and at least some of the Ru column pairs are misaligned with respect to the hcp layer. This leads to frustration in the terminating hcp layer of the metal, as can be observed directly in Fig. 1. To a first approximation, the price of lattice length manipulation can be calculated by computing the sum of the individual energy losses caused by separately compressing an ideal Ru metal slab and stretching an ideal SRO slab (Fig. 4) to their respective values necessary to create the reduced supercell shown in Fig. 2. We find this energy to be 8.54 eV. On the other hand, the energy loss due to non alignment of the Ru interface pair columns in the experimentally observed geometry can be upper bounded by sliding the Ru metal layers of the reduced geometry along the interface, thus moving the Ru pair.

FIG. 4. (color-online) (a) The 2.5-layer thick Sr$_2$RuO$_4$ slab with equivalent (010) surfaces used to compute the energy of (001) linear strain changing the $c$-lattice vector length from 12.9 Å to 13.52 Å while keeping the $a$ and $b$-vectors same as in bulk. (b) The 1.5-layer thick ruthenium metal slabs in its hcp structure with (001) surfaces used to compute the energy of planar compression. The $a$, $b$ lattice vectors were each reduced from 2.73 Å to 2.61 Å. In both calculations we used at least 15 Å of vacuum between repeated images.

FIG. 5. (color-online) A hypothetical interface between SRO [100] and Ru hcp [001] surfaces, created from the slabs in Fig. 4 by bringing them together gradually and allowing the atoms to relax till the optimum interlayer distance at the interface is reached. This geometry is similar to that in Fig. 2 except in the absence of the Ru interface columns. The hcp c-axis is parallel to the SRO [100] direction. Part of the next repeated image is shown for clarity.
be cleaved with a terminating SrO or RuO
ble that ours. In particular, the (001) surface of SRO can
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(001) surface, meandering Ru interface columns with the
in any interface between the SRO (100) surface and Ru
and compressing the constituent phases. It follows that
pair columns is 4

columns away from the potential valleys of the hcp layer,
until we reach an energy maximum.
The maximum cost of misalignment of the interface Ru
pair columns is 4.49 eV, less than the cost of stretching
and compressing the constituent phases. It follows that
in any interface between the SRO (100) surface and Ru
(001) surface, meandering Ru interface columns with the
experimentally observed periodicity is the most stable
structure.
As a final part of our stability argument, we consider
the possibility that there can be other types of interfaces
without these interface Ru columns which are more sta-
ble that ours. In particular, the (001) surface of SRO can
be cleaved with a terminating SrO or RuO₂ layer and its
interface with a ruthenium hcp layer can be conceived.
We show in Fig. 6 a commensurate geometry at the inter-
face, in which a 5 × 6 RuO₂ superstructure (defined along
the SRO a and b-axes respectively) is commensurate with a
7 × 5 superstructure of the metal, after accounting for
a 0.8 % uniaxial strain on the Ru metal. Most of the
atoms of each phase in this superlattice are randomly
oriented with those of the other phase and therefore each
layer at the interface will experience the laterally aver-
gaged potential of the other layer. This is arguably a small
energy gain of the order of a few tens of eV for each
SRO formula unit. In fact, any interface without the pe-
riodic meanders observed in our experiment is likely to be
disfavored for the same reason. A straightforward GGA
computation shows that our reduced structure is lower
in energy by 1.72 eV compared to the sum of energies of
a Ru metal slab similar to that shown in Fig. 4(b) and
the appropriate amount of bulk SRO, a surprising result.
The experimentally observed superlattice should be even
more stable. We conclude therefore that the observed
meandering interface is favored even over phase separa-
tion of the eutectic mixture between bulk SRO and Ru.
Therefore, we cannot think of any other interface which
can compete with the one observed by our STEM study.
Lastly, the following question arises. Since we find that
the observed interface lowers the energy with respect to
bulk SRO and a semi-infinite Ru metal, why the system
does not try to create more such interfaces and instead
it grows mesoscopic size inclusions. Indeed, our findings
indicate that the lowest energy state of such a system of
SRO with excess Ru metal should be a state with a high
density of such interfaces separated by a microscopic-size
length. However, the combined system was created un-
der non-equilibrium conditions of the eutectic mixture
which do not allow for the system to search for a global
lowest energy state. First, at a relatively short-time scale
the free energy is only locally minimized and, then, the
system freezes in a macroscopic state of domains which
require an overwhelmingly large amount of time to find
the state which is the global minimum. More specifically,
one a few layers of Ru metal have grown, it becomes lo-
cally energetically favorable for more Ru atoms from the
excess of Ru, to attach themselves to those existing Ru
metal layer. Forming another interface which combines a
simultaneous and coherent arrangement of many atoms
is a much slower process (i.e., a low entropy state) than
simply adding to the existing Ru metal layer an addi-
tional single Ru atom. This means that the path to the
actual ground state is “narrow” and requires a very slow
process and, as a result, the system gets stuck in other
metastable local free-energy minima. Thus, although a
high density of such interfaces is preferred by taking into
consideration just the energy of the system, the meander-
ting termination layer of SRO with intact RuO₂ octahedra
and interface Ru columns are long-range phenomena gen-
erally suppressed by the large entropy present in the high
temperature eutectic mixture.

C. Computational details
Spin-GGA computations were performed using plane-
d-wave basis set (cutoff of 540 eV) with the projected
augmented wave methodology²⁹ used to describe the
wavefunctions of the electrons as implemented in the
VASP package³⁰–³³, using the Perdew-Burke-Ernzerhof
(PBE) exchange correlation functional³⁴. The 4s, 4p,
5s electrons of strontium, the 5s, 4d, 4p, 4s electrons of
Ru and the 2s, 2p electrons of the oxygen were treated
as valence electrons. The Brillouin zone of the 128-
atoms supercell with the meandering interface geometry
(Fig. 2) and the 124-atoms supercell with flat interfaces

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FIG. 6. (color-online) A possible interface between (001) SRO
and hcp Ru metal with a 19.52 Å ×23.42 Å superlattice
where after a 0.8 % strain on the hcp plane, five planar unit
cells of RuO₂ is commensurate with seven unit cells of the
Ru metal in the SRO [001] direction and six unit cells of
RuO₂ is commensurate with five unit cells of the Ru metal
in the SRO [010] direction. Most of the atoms at the interface
are frustrated and experience the laterally averaged potential
leading to very little energy gain. Both SRO and Ru-metal
lattice vectors are shown.
(Fig. 5) were sampled with $1 \times 6 \times 4$ $k$-point grid, and 60 $k$-points were used to compute the electronic density of states (DOS). Increasing the $k$-point grid from $1 \times 6 \times 4$ to $1 \times 7 \times 5$ leads to a negligibly small change of the total energy of the meandering interface geometry by 0.04 eV and an increase of the moments of the magnetic ruthenium atoms by 0.08 $\mu_B$. The 70-atoms SRO slab (Fig. 4(a)) is 2.5 layers thick with symmetric $2 \times 1 b-c$ surfaces. We have used a tetragonal geometry with $b = 3.90$ Å and $c = 12.90$ Å and sampled the Brillouin zone with a $1 \times 8 \times 4$ $k$-point grid. For the 54 atoms Ru metal slab (Fig. 4(b)) which is 1.5 layers thick with a $6 \times 3 \times 1.5$ structure, we have used an hcp unit cell length of 2.739 Å and sampled the Brillouin zone with $4 \times 8 \times 1$ $k$-point grid. For both the slabs, we have used a vacuum layer at least 15 Å thick. All the supercells was structurally relaxed while keeping the cell shape and cell volume fixed until the forces were converged to less than 10 meV/Å for each ion.

III. ELECTRONIC PROPERTIES

![Orbital Projected DOS](image)

**FIG. 7.** (color-online) $Y_{100}$-projected density of states for a Ru atom from the interface column pair. The atom has a O$_2$ environment like in the rutile RuO$_2$ phase with bond angle of 115$^\circ$ and Ru-O bond length of 1.83 Å. On the other hand, it also neighbors the Ru metal closed-pack layer at the interface. Both these environments influence its electronic structure.

Our computed geometry (Fig. 2) shows a 1.8$^\circ$ rotation of the RuO$_6$ octahedron on the RuO$_2$ planes along with small amounts of buckling. We find no magnetic moments in the interface columns of Ru atoms and metallic phase Ru atoms, but strong magnetic moments in the Ru atoms ($M_{Ru} = 1.532 \mu_B$) in the SRO phase. GGA calculations have previously predicted$^{13}$ surface ferromagnetism in SRO where it was stabilized by a large (9$^\circ$) surface octahedra rotation and consequent band narrowing. To ensure that this is not purely an effect of the (001) strain, we have performed spin-GGA calculations of bulk SRO with stretched c-axis values. The octahedra rotations are absent and we find a ferromagnetic ground state but with much smaller magnetic moments ($M_{Ru} = 0.220 \mu_B$).

In the interface Ru atom columns, there are two different types of RuO$_2$ bonds in each pair. One has bond angle close to 90$^\circ$ and Ru-O bond length close to the planar Ru-O(1) bond length, whereas the other has bond angle $\sim$ 115$^\circ$ and Ru-O bond length $\sim$ 1.83 Å. Both Ru atoms lack the planar square lattice coordination and are expected to have different orbital structure compared to those in SRO. Indeed, we find significant $t_{2g}-e_g$ mixing in each of them. Figure 7 shows the density of states of the Ru atom which has a RuO$_2$ bond angle of $\sim$ 115$^\circ$. Both the $d_{x^2-y^2}$ and $d_{z^2}$ states are pulled down below the Fermi level and mixed with $t_{2g}$ orbitals. $t_{2g} - e_g$ mixing was found at the well-studied SrTiO$_3$/LaAlO$_4$ interface$^{36}$, where an $e_g$ splitting was caused by oxygen vacancy and gave rise to magnetic order. Here, it is caused by severe Ru-O hybridization and non planar RuO$_2$ geometry.

IV. IMPLICATIONS FOR SUPERCONDUCTIVITY

The observation that the “3-K” superconductivity is unconventional with the presence of a hysteresis loop$^{25}$, together with our findings could point to a possible coexistence of short-range ferromagnetic order and spin-triplet superconductivity$^{37-39}$, or presence of two dimensional unconventional superconductivity close to a ferromagnetic instability. In addition, an enhancement of the magnetic susceptibility on the interface of these inclusions with SRO should lead to an enhancement in the spin-triplet channel for pairing due to increased electron-paramagnon ferromagnetic spin fluctuations$^{33}$ coupling. While the spin-triplet superconducting order parameter might compete with the ferromagnetic order parameter, the p-wave pairing order parameter, which breaks time-reversal symmetry, could benefit from approaching closer to the ferromagnetic instability. We find that the volume of these micro-inclusions is of the order of $\sim$ 10 $\mu m^3$ and their surface is $\sim$ 50 $\mu m^2$. Therefore, the volume to surface ratio is about 2000 Å which is only about 200 times larger than the unit cell of the SRO along the [001] direction. If we consider the interface magnetic moments as magnetic impurities, the system is in the very dilute limit (of the order of 0.01 %), and it might seem hard to understand that these magnetic impurities would give rise to such a large effect on the superconducting transition temperature. It is already known$^{40}$ that approximately 0.7 % Co magnetic impurities in pure Sr$_2$RuO$_4$ lead to a long lived ferromagnetic state. Furthermore, the superconducting $T_C$ depends exponentially on the electron-paramagnon coupling, i.e., $k_B T_C \sim \hbar \omega_p \exp(-m^*/\lambda)$ where $\omega_p$ is the
paramagnon frequency, \( m^* \) is the electron effective mass enhancement and \( \lambda \) is a dimensionless measure of the electron-paramagnon coupling\(^{11}\). Thus, \( T_c \) is expected to be very sensitive to small changes in the electron-paramagnon coupling caused by enhanced ferromagnetic moments found by our DFT calculations at the interface with the Ru inclusions. However, the extremely low density of the moments makes it difficult to imagine that this is the primary reason for enhancement of \( T_c \). We find the following idea more appealing as a possible explanation for the enhancement of \( T_c \) in these Ru-inclusion rich SRO crystals.

Superconductivity is believed to arise from pairing within the RuO\(_2\) layers. The interlayer coupling between RuO\(_2\) planes is very weak which is expected to lead to large amplitude phase fluctuations of the order parameter as is the case of the Cuprate superconductivity\(^{41}\). These phase fluctuations should lower the value of the superconducting transition temperature.

In the case where inclusions are present, a remarkably ordered interface geometry between tetragonal unconventional superconductor Sr\(_2\)RuO\(_4\) and hexagonal closed pack metal Ru has been discovered as illustrated in both our STEM images of Fig. 1 and justified by means of our DFT calculations (Fig. 2) which also reveal the structure along the perpendicular direction as illustrated in our derived highly ordered structure of Fig. 3 (a direction which is hidden from any STEM study). These interfaces clearly should lead to an effective interlayer Josephson junction coupling of the superconducting order parameter which should reduce these phase fluctuations over. This coupling produced by these ordered inclusions should lead to an enhanced \( T_c \) as observed in the “3-K” phase. We believe that the reason for the enhancement of \( T_c \) due to the inclusions is different from the reason that causes the strain driven increase of \( T_c \) in pure bulk SRO as seen in Ref. 20. In the latter case the increase is due to the fact that the strain affects the symmetry character (i.e., \( p_x + ip_y \)) of the superconducting order parameter as argued in Ref. 20.

It has been shown experimentally\(^{23}\) that inclusions increase the interlayer coherence length and significantly reduce the anisotropy of superconductivity: \( \xi_{ab}(0)/\xi_c(0) = 3.6 \) in the “3-K” phase with metals inclusions as compared to 20 for the 1.5 K phase SRO.

V. CONCLUSIONS AND IMPLICATIONS

A remarkably ordered interface geometry between tetragonal unconventional superconductor Sr\(_2\)RuO\(_4\) and hexagonal closed pack metal Ru formed as metallic inclusions during the growth process of the superconductor has been revealed by STEM studies and has been investigated and understood in the present paper using DFT. The heterojunction is characterized by regular columns of Ru pairs in the SRO [001] direction and clean octahedra terminations of the ruthenate oxide. Using DFT, we have correctly reproduced the experimental structure including the positions of interface oxygen atoms and along directions hidden to any STEM study and investigated the electronic structure of the interface. We have found rotated octahedra, modified Ru d-orbitals and enhanced magnetic moments near the interface in the SRO phase. Application of GGA to magnetism should be taken with caution since it does not correctly account for correlations, but given the proximity to Stoner instability, it is possible that the interface is in or energetically very close to a ferromagnetic ground state.

Our study provides a possible explanation of the enhancement of the superconducting \( T_C \) when Ru metal inclusions are present. We find that these inclusions form microscopically well-ordered interfaces and structure. The interfaces acts as “ladder” which couple the superconducting order parameter of a large number of RuO\(_2\) SRO layers over a micrometer-size length. These inclusions should lead to an interlayer coupling which can significantly reduce the superconducting order parameter phase fluctuations, thereby increasing the superconducting critical temperature.

This observation opens up exciting prospects when a similar growth process is applied to the case of the cuprate superconductors. If these inclusions introduce an interlayer Josephson-Junction type coupling, we should expect a significant enhancement of the superconductivity critical temperature.

VI. ACKNOWLEDGMENTS

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