Superconductivity in the antiperovskite Dirac-metal oxide Sr$_3-x$SnO

Mohamed Oudah$^1$, Atsutoshi Ikeda$^1$, Jan Niklas Hausmann$^{1,2}$, Shingo Yonezawa$^1$, Toshiyuki Fukumoto$^3$, Shingo Kobayashi$^{3,4}$, Masatoshi Sato$^5$ & Yoshiteru Maeno$^1$

Investigations of perovskite oxides triggered by the discovery of high-temperature and unconventional superconductors have had crucial roles in stimulating and guiding the development of modern condensed-matter physics. Antiperovskite oxides are charge-inverted counterpart materials to perovskite oxides, with unusual negative ionic states of a constituent metal. No superconductivity was reported among the antiperovskite oxides so far. Here we present the first superconducting antiperovskite oxide Sr$_3-x$SnO with the transition temperature of around 5 K. Sr$_3$SnO possesses Dirac points in its electronic structure, and we propose from theoretical analysis a possibility of a topological odd-parity superconductivity analogous to the superfluid $^3$He-B in moderately hole-doped Sr$_3-x$SnO. We envision that this discovery of a new class of oxide superconductors will lead to a rapid progress in physics and chemistry of antiperovskite oxides consisting of unusual metallic anions.
Oxides with perovskite-based structures have had one of the central roles in condensed-matter research for decades. In particular, the discoveries of high-temperature superconductivity in cuprates and unconventional superconductivity in the ruthenate $\text{Sr}_2\text{RuO}_4$ (ref 2) have driven the science community to deepen the concepts of strongly correlated electron systems substantially. These research efforts led to the discoveries of novel phenomena also in cubic perovskite oxides that are in the base of these materials. Examples are colossal magnetoresistance, multiferroicity and superconductivity with the transition temperature $T_c$ of up to 30 K, reported for $\text{Ba}_0.6\text{K}_0.4\text{Bi}_0.3\text{O}_3$ (ref 5). This history of perovskites tells us that the finding of a new class of oxide superconductors has a potential to initiate unexplored research fields.

Perovskite oxides have their counterparts, antiperovskite oxides $A_3\text{BO}$ (or $\text{BOA}_3$), in which the position of metal and oxygen ions are reversed. Antiperovskite oxides were first found accidentally in an attempt to produce $\text{Sr}_3\text{SnO}$, which turned out to be stable only with inclusion of oxygen, forming $\text{Sr}_3\text{SnO}_3$ (ref 6). Upon this discovery, various $A_3\text{BO}$ with $A = \text{Ca, Sr, Ba and } B = \text{Sn, Pb}$ were synthesized and their structure identified. Antiperovskite oxides crystallize in cubic or pseudo-cubic structures with reverse occupancy of metal and oxygen relative to their perovskite counterparts, as illustrated in the inset of Fig. 1. Moreover, a recent study expanded antiperovskite oxides beyond the elements mentioned above. In the case of $\text{Sr}_3\text{SnO}$, the Sr–Sr distance of 3.548 Å is close to the Sr–Sr distance in the similarly coordinated $\text{Sr}_3\text{O}$, 3.650 Å (ref 8), and is shorter than that in pure Sr, 4.296 Å (ref 9). This comparison confirms that an oxidation state of $\text{Sr}^{2+}$ is realized in $\text{Sr}_3\text{SnO}$. With an assumption that O ions have $2–$ valency, we obtain a charge-balanced formula of $(\text{Sr}^{2+})_3(\text{Sn}^{4+})_3(\text{O}^{2–})_9$, indicating an unusual negative oxidation state of group-14 elements characteristic of antiperovskite oxides. The antiperovskite oxides were left relatively unexplored for some time, perhaps because of their instability in air. In particular, no superconductivity is reported among antiperovskite oxides. For a material related to antiperovskite oxides, the effect of interstitial oxygen on the superconducting properties of $\text{La}_3\text{In}$ ($T_c = 10$ K) has been reported. The range of oxygen content was suggested to be limited much below unity. Moreover, $T_c$ remained identical to that of $\text{La}_3\text{In}$ and just a strong reduction of the diamagnetic volume fraction was reported by adding oxygen. Thus it was not demonstrated that the antiperovskite $\text{La}_3\text{InO}$ is a bulk superconductor. We comment here that there have been reports on superconductivity in antiperovskite carbides, nitrides and phosphides in recent years, starting from the discovery in $\text{MgC}_3\text{Ni}_3$ ($T_c = 8$ K) (ref 11). These compounds have conventional valence states in contrast to antiperovskite oxides, and the superconductivity is attributed to ordinary phonon-mediated pairing among transition-metal $d$ electrons.

Recent band calculations for a closely related antiperovskite oxide $\text{Ca}_3\text{PbO}$ reveal slightly gapped three-dimensional Dirac cones in the very vicinity of the Fermi level, owing to the energy-level inversion of the Ca-3$d$ and Pb-6$p$ bands near the $\Gamma$ point. In particular, bands with the Dirac dispersion are dominant around the Fermi level, being ideal to investigate Dirac-electron properties. Also, it has been predicted that a class of topological crystalline insulators exists within antiperovskite oxides, and $\text{Sr}_3\text{SnO}$ lies on the border of the topological phase.

In this article, we present the evidence for bulk superconductivity in polycrystalline $\text{Sr}_3\text{SnO}$ samples through observation of zero resistivity and Meissner diamagnetism. Superconducting samples are found to have dominant hole carriers with the carrier density of $1 \times 10^{27}$ m$^{-3}$ at 300 K. We propose possible realization of a topological odd-parity superconducting state, which can have the condensation energy comparable to that of the ordinary s-wave superconductivity with the aid of the mixing of $\text{Sr}-4d$ and Sn-5$p$ orbitals (as outlined in Methods section "Topological superconductivity").

**Results**

**Sample preparation and characterization.** The powder X-ray diffraction of superconducting samples reveals cubic $\text{Sr}_3\text{SnO}$ to be dominant as presented in Fig. 1 but with some splitting in the peaks. The main phase has the lattice parameter $a = 5.1222$ Å and the minor phase $a = 5.1450$ Å. These values are compared with the reported value $a = 5.12$ Å for polycrystalline samples synthesized at 600–700 °C (ref 4) and 5.1394 Å for single crystals synthesized at temperatures up to 1,100 °C (ref 6). The phase splitting is most likely due to different Sr deficiencies in some part of the sample, as Sr partially evaporates during the reaction. In addition, a very small amount of Sn and other impurity phases containing Sr are present (marked with asterisks in Fig. 1).

![Figure 1](https://example.com/figure1.png)

**Figure 1 | Structure and the sign of carriers in $\text{Sr}_3\text{SnO}$.** (a) Powder X-ray diffraction spectrum of a superconductive $\text{Sr}_3\text{SnO}$ batch-A sample. The spectrum was taken at room temperature on a lightly crushed sample with Kapton film and vacuum grease protecting it from air. Some impurity peaks can be seen marked with asterisks. The inset compares the perovskite $\text{SrSnO}_3$ and antiperovskite $\text{Sr}_3\text{SnO}_3$, emphasizing the change in oxidation states: $\text{Sr}^{2+}$ corresponds to $\text{Sn}^{4+}$, $\text{Sn}^{3+}$ to $\text{O}^{2–}$, and $\text{O}^{2–}$ to $\text{Sr}^{2+}$. (b) Hall coefficient measured as a function of temperatures showing hole-like carriers for a batch-A sample.
features in X-ray diffraction are common in other batches. All the samples showing superconductivity had Sr deficiency, either caused by significant Sr evaporation during synthesis or by Sr-deficient starting composition (see Methods section). As stoichiometric Sr₃SnO does not show superconductivity, we conclude that a deficiency of strontium leads to superconductivity in this compound.

**Superconducting properties.** The resistivity of Sr₃₋ₓSnO exhibits a sharp drop with an onset of 4.9 K and zero resistivity below 4.5 K in zero field (Fig. 2a, batch C). Magnetic shielding of another sample from the same batch with an onset of 4.8 K is observed in the imaginary and real parts of the alternating current (AC) magnetic susceptibility χ′″ and χ′AC (Fig. 2b,c). The transition in the direct current magnetization M(T) obtained with zero-field-cooling processes is more pronounced than the curve for the field-cooling process, as typical for type-II superconductivity with flux pinning. A sizable magnetic-flux expulsion in M corresponding to the superconducting volume fraction of 32% at 2 K was observed for the same sample (Fig. 2d, Batch C). The M(T) of another sample with the onset of 4.8 K exhibits a volume fraction of 62% at 2 K (Fig. 2d, Batch D). A similar data set for a sample from a different batch is also presented in Supplementary Fig. 1. These results assure bulk superconductivity in Sr₃₋ₓSnO. The field dependence of M reveals hysteretic behaviour again characteristic for a type-II superconductor (Supplementary Fig. 2). We note that the χAC curve obtained with adiabatic demagnetization cooling down to 0.15 K exhibits an additional transition at 0.8 K (Supplementary Fig. 1b,c). As the 0.8 K transition is reproducible in all superconducting batches that we investigated down to 0.15 K, it probably originates from another superconducting phase of Sr₃₋ₓSnO with different stoichiometry. The transition in the specific heat C_p is not as pronounced due to the inevitably large contribution of the phonon-specific heat compared with the electronic contribution with the small Sommerfeld coefficient γ. Nevertheless, a tiny anomaly below 5.1 K is observed after subtraction of the phonon contribution. The expected specific-heat jump is about 1% of the total specific heat and is on the order of uncertainty in the present measurements.

The superconducting phase diagram is shown in Fig. 3. Here, T_c values were obtained from 10% and 50% resistivities shown in Fig. 2a. The upper critical field Hc₂ for T→0 is estimated to be μ0Hc₂(0) = 0.44 T, using the Wertheimer–Helfand–Hohenberg relation Hc₂(0) = −0.72T_c dHc₂/dT)|γ−Tc (ref. 17). This value corresponds to the Ginzburg–Landau (GL) coherence length ξGL(0) of 27 nm.

**Normal-state properties and electronic states.** The resistivity R(T) shows metallic behaviour from room temperature with a relatively high residual resistivity ratio of ~16 and a small residual resistivity of 62 μΩcm for a polycrystalline sample (Supplementary Fig. 3a). This contrasts with the semiconducting behaviour reported for Sr₃SnO thin films18,19. The temperature dependence of the Hall coefficient R_H (Fig. 1b) indicates that holes are the dominant carriers in the whole temperature range. The estimated carrier densities, if we assume a single hole band, are 4 × 10²⁷ m⁻³ at 5 K and 1 × 10²⁷ m⁻³ at 300 K. The
magnetic field dependence of the Hall resistance is shown in Supplementary Fig. 3b, and the transverse magnetoresistance is presented in Supplementary Fig. 3c,d.

Such high-carrier density is consistent with heavy hole doping owing to Sr deficiency (Methods section). For stoichiometric Sr3SnO, the electronic states near the Fermi level are influenced by the band inversion between Sr-4d and Sn-5p orbitals and the associated Dirac points near the Γ point, as shown in Fig. 4a. Upon hole doping, a Fermi surface (FS) originating from these Dirac points merges into one FS around the Γ point. This FS with a deformed-octahedral shape has an unusual orbital texture as shown in Fig. 4b. In addition, another hole pocket with orbital mixing centred at the Γ point appears inside (Supplementary Fig. 4). We note that a first-principles band calculation utilizing the Heyd–Scuseria–Ernzerhof screened Coulomb hybrid density functionals indicates yet another hole pocket around the R point. In contrast, neither of our calculations based on the Heyd–Scuseria–Ernzerhof functionals nor the Perdew–Burke–Ernzerhof generalized gradient approximation reproduces the R-point pocket (Supplementary Fig. 5).

Discussion
Besides being the first superconductor among the antiperovskite oxides, Sr3−xSnO possesses the prospect of topological superconductivity. When Cooper pairs are formed in Sr3−xSnO, their parity reflects the orbital texture of the underlying FS. Thus electrons on the FS portion with strong orbital mixing favour forming odd-parity and correspondingly spin-triplet pairs. This odd-parity state belongs to the same representation as that of the fully gapped superfluid 3He-B phase. As depicted in Fig. 4c, Cooper pairs can have either purely p or d−p mixed orbital character depending on the location on the outer and inner FSs. At present, we cannot discern the possibility that the hole FS around the R point, in the heavily hole-doped Sr3−xSnO, is the main origin of the observed superconductivity. Even in that case, it is expected that pairing amplitude appears on the FS originating from the Dirac points and leads to unconventional properties related to topological superconductivity. Techniques used to observe Majorana zero modes on the surface of In1−xSnxTe (ref. 22), a leading candidate for three-dimensional topological superconductors, may be adopted on Sr3−xSnO to prove topological superconductivity.

In this article, we report evidence for bulk superconductivity in Sr3−xSnO with an onset of about 5 K, marking the first superconductivity among antiperovskite oxides. Mirroring the rich variety of properties in perovskite oxides, the present work opens a door to superconductivity as well as other interesting phenomena in antiperovskite oxides with unusual metallic anions.

Methods
Sample synthesis
(1) Batches A, B and C. Bulk polycrystalline samples of Sr3−xSnO, approximately 0.5 g each batch, were synthesized by reaction of Sr chunk (Furuuchi, 99.9%) and SnO powder (Furuuchi, 99.9%) in an alumina crucible sealed inside a quartz tube under vacuum. Preparations of synthesis were performed inside an Ar-filled glove box. The sealed quartz tubes were heated to 800 °C and kept at 800 °C for 3 h. Then the tubes were immediately quenched in water and opened inside the glove box. The obtained samples were stored and prepared for measurements in the glove box. A crude estimation of the amount of evaporated strontium by weight in batches A, B and C indicates that it was about 18% of the starting strontium amount.
(2) Batch D. In further investigations on the synthesis, we observed that the evaporation of strontium can be suppressed to <1% if the reaction was carried out in glass tubes that were sealed under 0.3 bar of argon pressure at room temperature instead of vacuum. Batch D was synthesized in this way with Sr2.46SnO as starting composition instead of Sr3SnO.
(3) Batch E. An excess of 25% strontium was used and the glass tube was sealed under vacuum for synthesis of batch E. For this batch, a 100% yield of Sr2.46SnO by weight with respect to the starting quantity of SnO was obtained. This batch E was considered an almost stoichiometric Sr3SnO phase. A sample from batch E, with approximately stoichiometric composition, showed semiconducting resistivity behaviour down to low temperature, with an anomaly at 4 K, suggesting an inclusion of a small superconducting region. However, in the magnetic measurement, this sample did not show evidence of superconductivity down to 0.15 K. The observed semiconducting behaviour agrees with the result from Sr3SnO thin-film reports and supports our claim that the Fermi level is shifted down in the bulk superconducting samples.

Figure 4 | Orbital texture and possible Cooper pair symmetry of Sr3−xSnO. (a) Band structure of Sr3SnO from tight-binding calculations with inverted orbital character and a Dirac point near the Γ point on each Γ–X line. Parameters are obtained by fitting to the first-principles calculation. Inset shows the cubic Brillouin zone. (b) Orbital texture of the Fermi surface (FS) around the Γ point, reflecting the band inversion. The colour represents the degree of mixing of Sn-5p and Sr-4d orbital wavefunctions ψp and ψd at each k point on the FS. The red and black colours represent pure p and dominant d, respectively. Orbital mixing on the outer FS is strongest along the Γ–M direction, while the p orbital dominates in the Γ–X direction. (c) Possible Cooper pair symmetries. If superconducting symmetry is dictated by the pairing in the blue region on the FS, odd-parity spin-triplet pairing is favoured owing to orbital mixing. In case it is dictated by the red region, even-parity spin-singlet pairing is favoured.
Performed by Hsieh

We confirmed that the sample degradation is negligible with this setup within typical measurement time of 200 min. A broad X-ray diffraction peak originating from the Kaption film was observed only below 20 = 20. Structure refinement was performed using TOPAS package (Bruker AXS, Version 4–2).

Characterization of superconductivity. Transport, AC magnetic susceptibility and heat capacity measurements were carried out in a commercial apparatus (Quantum Design, PPMS). For the resistivity and Hall coefficient measurements, a five-probe method was typically employed from 1.8 to 300 K with fields up to 5 T. On a sample with a typical size of 1.8 x 1.8 x 0.6 mm3, 50–μm-diameter gold wires were attached using silver epoxy (EPOXY TECHNOLOGY, H20E) inside a He-filled glove box. The samples were protected from exposure to air with vacuum grease (Apirone, N-grease) before taken out from the glove box. The AC susceptibility was measured using a small superconducting coil compatible with the PPMS and its adiabatic demagnetization refrigerator option. The specific heat of a piece of a sample covered with the grease was measured using a relaxation-time method using the PPMS. Additional small amount of grease, necessary to achieve good thermal contact to the sample, was applied to the sample stage during the addenda measurement as well. The addenda heat capacity was measured with and without the magnetic field to perform proper subtraction to obtain sample heat capacity.

The direct current magnetization M was measured using a commercial SQUID magnetometer (Quantum Design, MPMS). Samples were sealed inside plastic capsules under Ar environment. Degaussing of PPMS and MPMS prior to measurements ensured the accuracy of the applied field values. The remnant field inside the MPMS was occasionally measured using a Pb (99.9999%) reference structure.

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Author contributions

Y.M. designed the project; S.Y. supervised most aspects of the experiments; M.O., A.I., S.Y. and M.S. performed band calculations and theoretical analysis of the pairing symmetry;
M.O., A.I., J.N.H., S.Y., M.S. and Y.M. wrote the manuscript with contributions from T.F. and S.K.

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