

The observation of bulk superconductivity in rhombohedral ReO_3 under pressure

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ABSTRACT

Understanding how lattice geometry enables superconductivity in oxides remains a central challenge. Here, we report a systematic study of ReO_3 up to 80 GPa. Synchrotron x-ray diffraction, Raman spectroscopy, electrical transport, dc magnetic susceptibility, and first-principles calculations establish a sequence of pressure-induced structural transitions, from cubic $Pm\bar{3}m$ to $Im\bar{3}$ followed by the emergence of a rhombohedral $R3c$ phase accompanied by bulk superconductivity with a maximum $T_{c, \text{onset}} \sim 17.5$ K. DC magnetic susceptibility and trapped-flux magnetization measurements demonstrate that bulk superconductivity is confined to the pressure range where $R3c$ phase is dominant. Density functional theory calculations show strong electron-phonon coupling in the $hR24-R3c$ structure, with substantial contributions from both low-frequency Re vibrations and high-frequency oxygen-related phonon modes, yielding a calculated T_c comparable with the experiment. Upon further compression above ~ 35 –40 GPa, powder X-ray diffraction results indicate a symmetry-lowering structural transition. Whereas the experimental diffraction patterns can be best described by a rhombohedral-derived $R32$ -like average distortion with effective enlargement of the crystallographic unit cell, enthalpy calculations identify a lower-symmetry $mP16-P2/c$ structure driven by a phonon instability of the $R3c$ phase. This reconstructed higher-coordination phase has a reduced density of states at the Fermi level, weaker electron-phonon coupling, and a much lower calculated T_c , providing a microscopic explanation for the loss of bulk superconductivity in the higher-pressure phase. These results show that bulk superconductivity is stabilized within the rhombohedral structure, where pressure-induced lattice reconstruction supports enhanced electron-phonon coupling through cooperative Re-O lattice dynamics.

1. Introduction

Rhenium trioxide (ReO_3) is one of the deceptively simple ABX_3 perovskites with an unoccupied A-cation site, where strong Re-5d–O-2p hybridization leads to textbook lattice dynamics and unusual transport properties [1]. Corner-sharing ReO_6 octahedra support rigid-unit tilts and a soft M_3 phonon mode that underpins its negative thermal expansion (NTE) and tilt-driven pressure-induced structural transitions [2,3]. At ambient pressure, ReO_3 is in the cubic $Pm\bar{3}m$ structure. Recent pressure dependent neutron/X-ray/Raman work shows that above

~ 0.7 GPa a cubic $Im\bar{3}$ phase is stable to at least ~ 15 GPa and that several earlier noncubic assignments arose from high-flux X-ray-induced artifacts and/or non-hydrostaticity [4] – a methodological point that is crucial for interpreting emergent states in compressed ReO_3 .

At ambient pressure, in the $Pm\bar{3}m$ structure, ReO_3 remains non-superconducting down to 20 mK and has a relatively weak EPC constant of $\lambda \approx 0.3$ [5]. This behavior contrasts with the pressure-stabilized rhombohedral phase, in which structural reconstruction substantially modifies both the electronic structure and phonon-mediated coupling. In addition, ReO_3 displays extremely large magnetoresistance (XMR)

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governed by perfect carrier compensation for $H \parallel c$ and by open-orbit trajectories near $\theta \approx 15^\circ$ [6], underscoring the primacy of Fermi-surface geometry to magnetotransport properties, a transport regime that favors high mobility but not SC, such as was found recently in other binary compounds such as WTe_2 [7], LaBi [8], LaSb_2 [9], and Re_3Ge_7 [10]. Based on these observations, we suggest that the compression could rearrange the oxygen lattice of ReO_3 and thereby boost EPC and enabling the emergence of a SC dome in the high-pressure rhombohedral phase (while the XMR fingerprints weaken).

Beyond these observations, Shan et al. recently reported that in the rhombohedral-I (R-I) phase (≈ 12 – 39 GPa) a dome-shaped SC T_c peaking near ~ 17 K at ~ 30 GPa develops, advancing the view that oxygen-lattice vibrations in nearly close-packed O-layers supply a light-element-dominated EPC, an oxide-based analogue of hydride SC [11]. This perspective resonates with the design logic of superhydrides and other light-element SCs and potentially makes ReO_3 a conceptual bridge between metallic oxides and hydride-like phonon-mediated SC [1,11].

Several questions nevertheless remain regarding the superconducting (SC) and structural evolution of ReO_3 under high pressure. First, the pressure range over which SC is in bulk nature, rather than filamentary or percolative, has not been fully clarified. Second, the microscopic origin of the higher-pressure structural reconstruction, and its connection to the suppression of SC remains to be further understood. In particular, whether the high-pressure state corresponds primarily to a symmetry-lowering distortion of the rhombohedral phase or to a more substantial oxygen-framework reconstruction involving changes in Re-O coordination remains under active investigation.

In this work, we present a comprehensive, high-pressure investigation of ReO_3 that establishes a unified relation between structural evolution, electron–phonon coupling, and SC properties across an extended pressure-temperature space. By combining synchrotron powder X-ray diffraction, Raman spectroscopy, electrical transport, dc magnetization measurements, and first-principles calculations, we map out a sequence of pressure-induced structural transitions and correlate them directly with phonon behavior, electronic structural responses, and SC properties. We demonstrate that bulk SC is stabilized within the rhombohedral phase, where cooperative octahedral rotations are correlated with enhanced EPC involving both Re- and O-associated phonon modes. First-principles calculations reveal strong electron-phonon coupling in the

$R3c$ phase, with substantial contributions from both low-frequency Re-associated modes and high-frequency oxygen-related modes, yielding a calculated SC transition temperature comparable to experimental results. Upon further compression, a symmetry-lowering structural reconstruction suppresses the bulk SC. Whereas the experimental diffraction patterns can be best described by an $R32$ -like average distortion, enthalpy calculations instead predict a lower-symmetry $mP16$ - $P2/c$ phase driven by phonon instability of the rhombohedral state. This reconstructed higher-coordination phase has a reduced density of states at the Fermi level, weaker EPC, and a much lower calculated T_c , providing a microscopic explanation for the loss of bulk SC in the higher-pressure phase. In addition, we uncover robust NTE across multiple pressure-stabilized phases and identify a curious low-temperature volume anomaly below 35 K that is probably related to the SC regime, potentially signaling enhanced lattice instability in proximity to the high-pressure symmetry-breaking transition. Together, these results highlight the central role of lattice symmetry, oxygen-framework reconstruction, and EPC in governing SC in compressed ReO_3 and demonstrate pressure as a clean tuning parameter for engineering emergent quantum states in simple 5d oxides.

2. Results and discussion

The compiled, pressure-driven phase diagram is summarized in Fig. 1, demonstrating the electronic, magnetic, structural, and phonon vibrational properties of ReO_3 . The vertical dashed lines in Fig. 1 mark

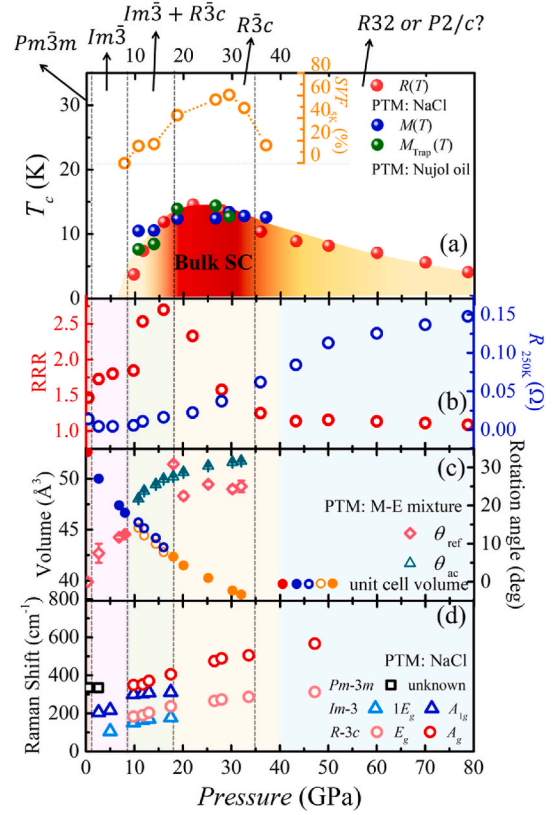


Fig. 1. Pressure dependence of electronic, magnetic, structural, and Raman properties of ReO_3 . The pressure dependence of (a) superconducting transition temperature T_c ; (b) left: residual resistance ratio, $R_{250\text{K}}/R_{20\text{K}}$, and right: resistance at 250 K; (c) left: unit cell volume estimated from the high-pressure x-ray diffraction measurement, with different colors of circles marking the evolution of the unit cell volume for five pressure regions, filled symbols represent single-phase region ($Im\bar{3}$ or $R3c$), open symbols for mixed-phase regions ($Im\bar{3}$ and $R3c$); and right: rotation angle of the ReO_6 octahedra, in which θ_{ref} is extracted from the refined structures and $\theta_{\text{ac}} = \cos^{-1}(\sqrt{6}a/c)$ assumes rigid ReO_6 octahedra rotation; and (d) Raman mode frequencies. Dashed lines and different color areas mark the phase boundaries and different structures determined from PXRD measurements with the structural phases labeled above the panel (a). The uncertainty in T_c arising from the temperature resolution and the determination criterion is smaller than the symbol size. The pressure values were determined at room temperature, and the pressure uncertainty is affected by pressure gradients and the protocol-dependent pressure drift upon cooling.

the phase boundaries identified primarily from powder X-ray diffraction (PXRD) measurements. These boundaries are consistent with the transport, magnetization, and Raman data. Whereas minor offsets in the critical pressures are unavoidable due to the use of different pressure-transmitting media (PTMs), manometers, criteria, and measurement temperatures, the overall interpretation of the phase diagram remains robust. Five distinct pressure regimes can be identified, spanning the low-pressure $Pm\bar{3}m$ cubic phase, an intermediate pressure distorted $Im\bar{3}$ cubic phase and two-phase coexistence region ($Im\bar{3}$ cubic and $R3c$ rhombohedral), the fully developed rhombohedral $R3c$ phase, and a higher-pressure phase proposed on the basis of both experimental observations and theoretical analysis. These regimes are corroborated by clearly defined discontinuities in the RRR, changes in the resistance isotherms (e.g., at 250 K), rotation angle of the ReO_3 octahedra and the emergence, splitting, and suppression of Raman-active phonon modes.

Viewed from a microscopic perspective, the phase diagram shown in Fig. 1 is most naturally organized by the progressive rotation and distortion of corner-sharing ReO_6 octahedra. Increasing pressure

incrementally reconstructs the oxygen sublattice and its coupling to the electronic degrees of freedom, with the octahedral rotation angle acting as a measure of how the lattice responds to pressure. In the cubic phases ($Pm\bar{3}m$ to $Im\bar{3}$), ReO_3 remains non-superconducting. Cooperative octahedral rotation gradually stabilizes the rhombohedral $R\bar{3}c$ structure, in which the oxygen layers evolve toward a nearly hexagonal close-packed configuration. Bulk superconductivity (SC) emerges exclusively within this phase and follows a dome-shaped pressure dependence, with T_c increasing systematically with the rotation angle and reaching its maximum near a critical angle of $\sim 30^\circ$, where the structural distortion is optimized. Upon further compression above ~ 35 GPa, our indexing suggests an effective doubling of the lattice parameters, along all crystallographic directions. Such a reconstruction of the real-space unit cell is expected to strongly modify the Brillouin-zone topology and electronic band structure through zone folding, leading to a redistribution of the electronic density of states at the Fermi level and a disruption of the phonon modes that optimally couple to the electrons. As a result, the delicate balance between lattice geometry, oxygen-dominated phonons, and EPC established in the $R\bar{3}c$ phase could be significantly altered, providing a reasonable explanation for the suppression of SC at the highest pressures.

Fig. 1(a) additionally shows a clear distinction between the SC dome inferred from transport measurements and the narrower pressure window in which bulk SC is delineated by magnetization measurements. Although the resistive feature of SC persists over a broad pressure range, magnetic susceptibility measurements reveal a substantial shielding fraction only between ~ 20 and 31 GPa, coinciding with the pressure interval where the $R\bar{3}c$ phase is structurally dominant. Below this range, SC is suppressed by phase coexistence, while above it, increasing structural complexity and pressure gradients destabilize the bulk SC state.

Fig. 2(a) presents PXRD patterns obtained on ReO_3 for pressures ranging from 0.3 to 52 GPa. Five distinct regions are identified: i) near ambient pressure, $P \leq 0.3$ GPa, ReO_3 exhibits cubic symmetry with $Pm\bar{3}m$ (space group (SG) # 221); ii) for $2.3 < P < 8$ GPa, weak reflections appear between the main peaks of $Pm\bar{3}m$ phase, and the patterns were indexed to cubic $Im\bar{3}$ symmetry (SG #204), see top panel of Fig. 2(b); iii) above 10 GPa, a rhombohedral phase with rhombohedral $R\bar{3}c$ symmetry (SG #161) emerges, and for pressures up to 16 GPa, both $Im\bar{3}$ and $R\bar{3}c$ phases are indexed, as shown in the middle panel of Fig. 2(b) at 12 GPa; iv) for $18 < P < 32$ GPa, only the rhombohedral $R\bar{3}c$ phase is observed, as illustrated by the refinement of the 25 GPa data in the bottom panel of Fig. 2(b); and v) at high pressures, above 34 GPa, new peaks appear at $2\theta \approx 8$ deg, while high-angle peaks disappear, suggesting the emergence of a new phase, that we are not able to unambiguously identify. Table S1 provides crystallographic information of the $R\bar{3}c$ phase at 25.1 GPa.

It is noteworthy that up to 10 GPa, our data could be readily indexed by $Pm\bar{3}m$ or $Im\bar{3}$ cubic phases, with no evidence of monoclinic $C2/c$ [12, 13] or tetragonal $P4/mbm$ symmetries [14], in agreement with recent works on ReO_3 [11]. Recently, Efthimiopoulos et al. also suggested that the $Im\bar{3}$ phase is stable at even higher pressures, $P \approx 15$ GPa, attributing the emergence of new peaks above 10 GPa to radiation damage to the samples in a high-flux synchrotron source [4]. Our data are not consistent with this scenario, in fact the main reflections of $Im\bar{3}$ phase decrease in intensity above ~ 10 GPa and completely vanish above 16 GPa, with the $R\bar{3}c$ phase being stable up to 32 GPa. Furthermore, no anomalous peak broadening was found above 10 GPa, as would be expected for damaged samples that were still illuminated by the X-ray beam.

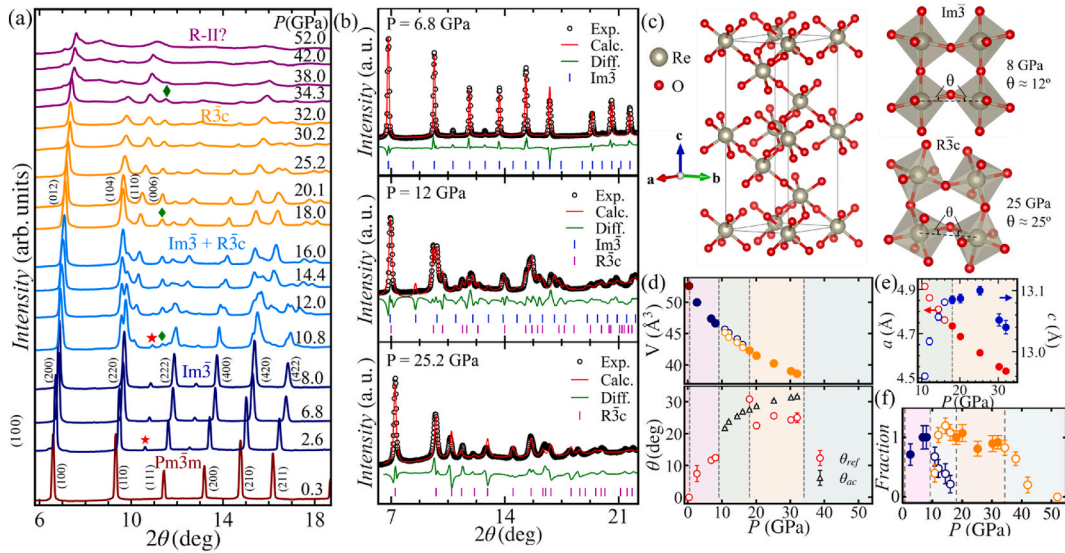


Fig. 2. Pressure induced structural phase transitions of ReO_3 . (a) Room temperature powder X-ray diffraction patterns obtained on ReO_3 samples at various pressures from 0.3 to 52 GPa (run 1). The synchrotron X-ray wavelength is 0.4306 Å. The red star and green diamond highlight isolated peaks from $Im\bar{3}$ and $R\bar{3}c$ phases, respectively. (b) Rietveld refinement of PXRD patterns of $Im\bar{3}$ (top panel) and $R\bar{3}c$ (bottom panel) phases at 6.8 GPa and 25.2 GPa, respectively. In the middle panel, a Le Bail fit is shown for the two-phase mixture of $Im\bar{3}$ and $R\bar{3}c$ at 12 GPa. (c) Crystal structure of the rhombohedral $R\bar{3}c$ phase, with corner-shared ReO_6 octahedra. $Im\bar{3}$ and $R\bar{3}c$ phases are connected by octahedral rotations, with the rotation angle θ increasing from 12 to 25 deg between 8 GPa and 25 GPa. (d) Pressure dependence of volume per formula unit V (top panel) and octahedra rotation angle θ (bottom panel). The rotation angle was determined from the refined structures θ_{ref} (in red) and also estimated from lattice parameters $\theta_{ac} = \cos^{-1}(\sqrt{6}a/c)$ (in black). (e) Pressure dependences of the refined lattice constants a and c in the $R\bar{3}c$ phase. (f) Phase fractions p in each pressure range. p is estimated by the maximum intensity of the isolated peaks highlighted in (a) normalized by the corresponding intensity observed in the single-phase regions. Solid and open symbols show data points in single- or mixed-phase regions, respectively.

The pressure evolution of the ReO_6 framework can be described more quantitatively by the octahedral rotation angle θ , as shown in Fig. 2(d). Here, θ was evaluated in two ways: θ_{ref} determined from the refined structural model and θ_{lat} estimated from the pressure-dependent lattice parameters under a rigid-octahedron approximation. θ_{ref} and θ_{lat} provide consistent evidence for progressive rotation of the corner-sharing ReO_6 framework upon compression. In the low-pressure cubic phases, θ is small. Upon entering the rhombohedral phase, θ increases rapidly, reflecting cooperative tilting of the ReO_6 octahedra. In the pressure range where bulk SC is established by both electrical transport and magnetic susceptibility measurements, θ already approaches the critical value of $\sim 30^\circ$. The lattice-parameter-derived θ_{lat} shows a weak continued increase with pressure within this bulk-SC region, whereas θ_{ref} obtained directly from the refined structures remains nearly pressure independent, staying close to $\sim 30^\circ$ within the uncertainty of the refinement. This behavior suggests that the rhombohedral ReO_6 framework has approached a geometrically optimized/saturated, strongly rotated configuration, rather than undergoing a large additional internal distortion of individual ReO_6 octahedra.

The sequence of structural transitions $Pm\bar{3}m \rightarrow Im\bar{3} \rightarrow R\bar{3}c$ is consistent with that reported in Ref. [11]. In that work, the authors suggested that the high-pressure phase, $P > 34$ GPa, also has rhombohedral symmetry (indicated by R-II). Within the resolution of our diffraction data in the first run, however, the patterns collected in this pressure range could not be unambiguously indexed. A second experimental run employing neon as the PTM yields significantly improved diffraction quality at high pressures (Fig. s1). For example, the diffraction pattern at 55 GPa can be indexed with several candidate symmetries (Figs. s3 and s4) among which an $R\bar{3}2$ structure (SG #155) dominated by the displacement modes $L1$ of $R\bar{3}c$ (notation from ISODISTORT [15,16]) provides the best agreement. This structure is associated with a doubling of the lattice parameters along all crystallographic directions.

Fig. 3(a) plots the density functional theory (DFT)-calculated enthalpy difference $\Delta H(P)$ of the different ReO_3 crystal structures with respect to the ambient phase of $cP4-Pm\bar{3}m$ in space group #221. The calculated structural phase transitions are $cI32-Im\bar{3}$ (#204) at 5.8 GPa and $hR24-R\bar{3}c$ (#167) at 18.2 GPa, which agree reasonably well with the experimental observations. The structural change involves the bending of the Re-O-Re linear bond with increasing pressure. With even higher pressure, we predict the $mP16-P2/c$ (#13) structure at 43.0 GPa by following the imaginary phonon mode of $hR24-R\bar{3}c$ at high pressure. The distinct structural feature of $mP16-P2/c$ is the increased Re-O coordination number to 7 from 6 of the ideal and distorted ReO_6 octahedron units in the lower pressure structures as shown in Fig. 3(d and e). Consistent with this theoretical prediction, the 55 GPa diffraction pattern from run 2 can also be reasonably fitted by the $mP16-P2/c$ phase, as shown in Fig. s4. The increase in local Re-O coordination reflects a pressure-driven reconstruction toward a denser local environment, a structural tendency broadly reminiscent of high-pressure SC metal hydrides. However, in ReO_3 , this denser higher-coordination phase does not enhance SC; instead, SC is suppressed, motivating the following comparison of the electronic structure, phonon spectrum, and EPC between $hR24-R\bar{3}c$ phase and the $mP16-P2/c$ phase.

We thus calculated the phonon spectra and EPC using density functional perturbation theory (DFPT), and calculated the EPC spectra using the isotropic Eliashberg approximation, with the SC T_c estimated using the McMillan-Allen-Dynes formula. Fig. 4(a) plots the phonon spectra of the SC $hR24-R\bar{3}c$ structure at 40 GPa with atomic projections, which shows the low frequency modes < 7 THz are predominantly associated with Re motion, whereas predominantly O-associated modes are the higher-frequency modes. In Fig. 4(b), the same phonon spectra are

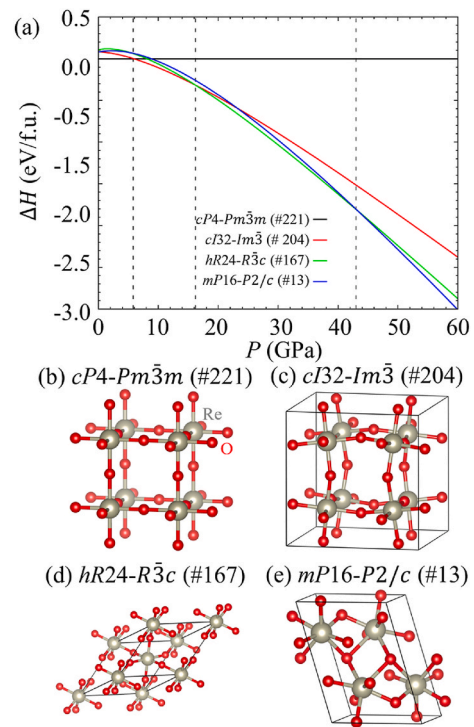


Fig. 3. Calculated structural phase transitions of ReO_3 in DFT. (a) Enthalpy difference ΔH as a function of pressure (P) with respect to the ambient phase of $cP4-Pm\bar{3}m$ in space group 221. The calculated structural phase transitions are $cI32-Im\bar{3}$ (#204) at 5.8 GPa, $hR24-R\bar{3}c$ (#167) at 18.2 GPa and $mP16-P2/c$ (#13) at 43.0 GPa. The corresponding crystal structures are displayed in (b) $cP4-Pm\bar{3}m$ (#221), (c) $cI32-Im\bar{3}$ (#204), (d) $hR24-R\bar{3}c$ (#167) and (e) $mP16-P2/c$ (#13).

decorated with mode-resolved EPC $\lambda_{qv}(\omega)$ projection (green dots), which shows large EPC for the low frequency modes. This behavior can also be seen in the Eliashberg spectral function $\alpha^2F(\omega)$ and its integration (dashed line) in Fig. 4(c). The contribution to the overall EPC λ is already at 0.75 for Re-dominated low frequency modes < 7 THz, but the O-dominated modes also make an important contribution of 0.47 to λ at high frequency. Future high-pressure oxygen-isotope-effect measurements would provide a valuable direct test of the contribution of oxygen-associated phonons to SC in ReO_3 . With the calculated $\omega_{\text{log}} = 308.2$ K and using the Coulomb potential of 0.16, the estimated $T_c = 20.1$ K for $hR24-R\bar{3}c$ at 40 GPa is in reasonable agreement with experiment.

To examine the pressure evolution of EPC within the $hR24/R\bar{3}c$ phase, we further calculated λ , ω_{log} , T_c , and the Re-O-Re bond angle at selected pressures (Fig. s5). With increasing pressure from 20 to 40 GPa, λ increases from approximately 0.61 to 1.22, while the Re-O-Re angle decreases from approximately 139° to 131° , establishing a quantitative correlation between enhanced octahedral rotation and stronger EPC. However, T_c does not scale monotonically with either λ or the bond angle alone. The increase in λ is accompanied by a decrease in ω_{log} , and the competition between these two quantities produces the calculated broad dome-like T_c evolution.

Now we compare the electronic structure, phonon spectrum, and EPC of the SC $hR24-R\bar{3}c$ phase and the higher-pressure $mP16-P2/c$ phase. As shown in Fig. 4(d), $mP16-P2/c$ phase at 50 GPa has a broader electronic density of states (DOS) due to shorter Re-O bonds at higher pressure than $hR24-R\bar{3}c$ phase at 40 GPa. Most noticeable is the decrease of the DOS at the Fermi energy (E_F), which also closes the pseudo gap

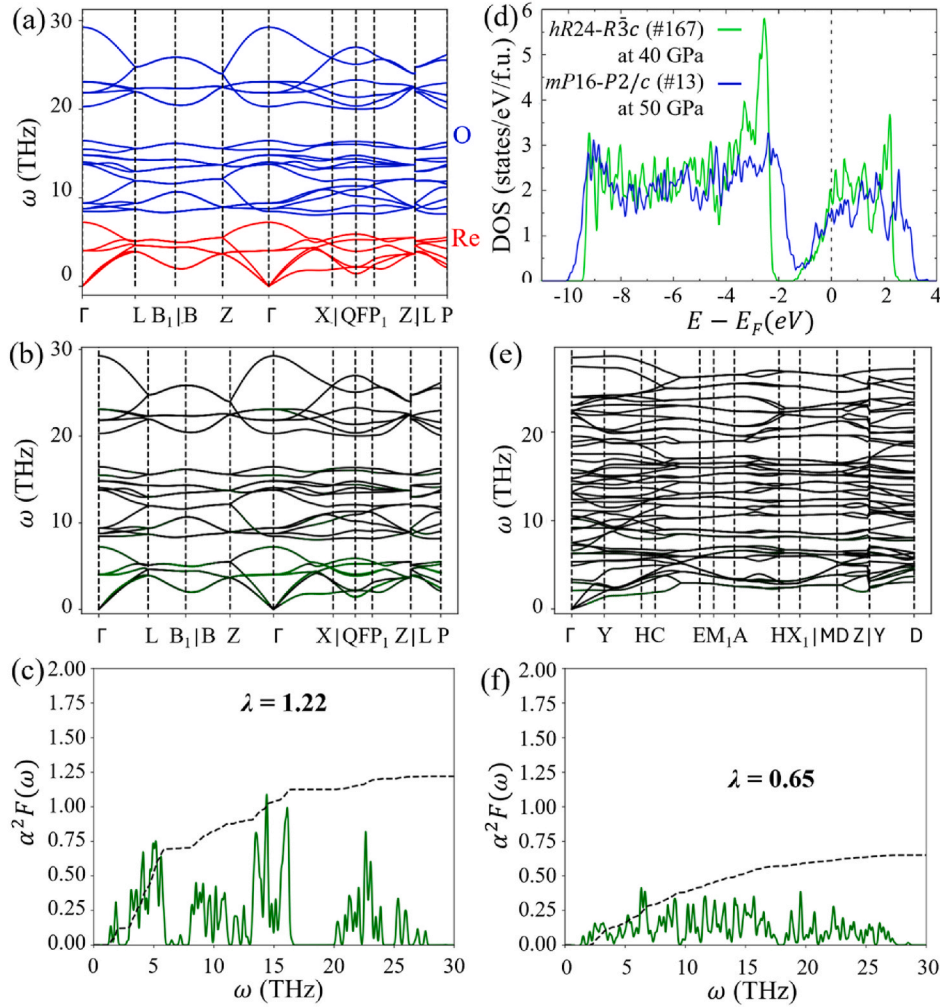


Fig. 4. Calculated phonon and electron-phonon coupling (EPC) spectra of ReO_3 in *hR24* (167) at 40 GPa and *mP16* (13) at 50 GPa. (a) Phonon spectra with atomic projection, (b) phonon spectra with mode-resolved EPC $\lambda_{qv}(\omega)$ projection (green dots) and (c) isotropic Eliashberg spectral function $\alpha^2F(\omega)$ and its integration (dashed line) in *hR24-R3c* (#167) at 40 GPa. (d) Electronic density of states (DOS) comparison of *mP16-P2/c* (#13) at 50 GPa vs. *hR24-R3c* (#167) at 40 GPa. (e) Phonon spectra with $\lambda_{qv}(\omega)$ projection and (f) $\alpha^2F(\omega)$ of *mP16-P2/c* (#13) at 50 GPa. The estimated phonon-mediated superconducting critical temperature (T_c) of ReO_3 is 20.1 K with an overall EPC $\lambda = 1.22$ for *hR24-R3c* (#167) at 40 GPa and 5.8 K with $\lambda = 0.65$ for *mP16-P2/c* (#13) at 50 GPa.

region around $E_F - 2$ eV. For the phonon spectra in Fig. 4(e), there are smaller mode-resolved EPC $\lambda_{qv}(\omega)$ projection than the *hR24-R3c* in Fig. 4(b), although with the greater number of modes due to lower symmetry. The overall EPC λ is reduced to 0.65 as plotted in Fig. 4(f). The estimated T_c is reduced to 5.8 K for the *mP16-P2/c* at 50 GPa. This behavior of decreasing T_c across the structural phase transition from *hR24-R3c* to a lower symmetry structure at higher pressure agrees well with the experimental observations and can be explained with the structural change of *mP16-P2/c* with the increased Re-O coordination number reducing both the DOS at E_F and the overall EPC strength.

Fig. 5 presents the Raman spectra at selected pressures, and the pressure evolution of the Raman mode frequencies. The optical micrographs collected at the corresponding pressures are shown in Fig. S6. Here, we emphasize that linewidths in DAC micro-Raman spectra on powders are systematically broadened by orientational averaging, grain-to-grain stress/strain distributions, and finite pressure gradients within the probed spot; therefore, we focus on the emergence/suppression and pressure evolution of dominant spectral features rather than peak sharpness. Importantly, the pressure-induced evolution of first-order Raman-active phonon modes in ReO_3 agrees well with the multi-step

structural phase transitions shown by PXRD results. Whereas minor differences in the critical pressures may arise from the use of different PTMs, the overall Raman behavior remains qualitatively consistent with the diffraction results.

At 0.5 GPa, ReO_3 in its cubic $Pm\bar{3}m$ structure exhibits an overall reddish optical contrast, as shown in Fig. S6 (the apparent color difference may be affected by the camera response, white balance, illumination conditions and the DAC optical path). The optical image, however, reveals localized grayish regions across the chamber. This non-uniform color originates from the granular nature of the loosely packed powder at very low pressure. Incomplete compaction leads to interparticle voids and local variations in optical path length, causing spatial differences in light scattering and reflectivity. Therefore, color variations at 0.5 GPa most likely reflect powder packing effects rather than the chemical inhomogeneity.

According to group-theoretical analysis for the cubic $Pm\bar{3}m$ symmetry, no first-order Raman-active phonons are allowed at the Γ point [17]. Consistent with this expectation, the Raman spectrum at 0.5 GPa does not exhibit well-defined symmetry-resolved phonon modes. Instead, a broad feature centered near $\sim 340 \text{ cm}^{-1}$ is observed, as shown in Fig. 5(a). This broad feature is more likely attributed to

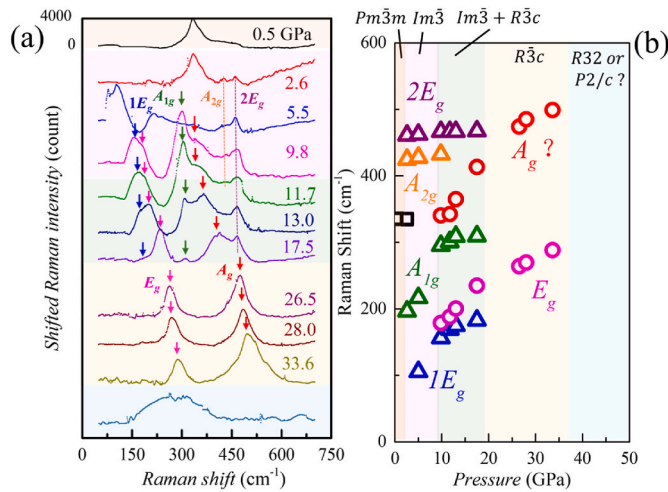


Fig. 5. (a) Room-temperature Raman spectra of ReO_3 at selected pressures ($\lambda = 633$ nm), vertically offset for clarity. The optical micrographs and Raman measurements were performed in the same run as the transport experiments. Colored arrows and dashed lines track the pressure evolution of symmetry-allowed phonon modes. In the $Im\bar{3}$ phase, blue and green arrows indicate the low-frequency modes ($1E_g$ and A_{1g}), while orange and purple dashed lines mark higher-frequency modes (A_{2g} and $2E_g$, at ~ 450 cm^{-1}). Pink and red arrows indicate emergence of the corresponding phonon modes (possibly E_g and A_g) in $R\bar{3}c$ phase and their pressure evolution. (b) Pressure dependence of the Raman mode frequencies extracted from (a). Symbol colors correspond to the arrows in panel (a). The black open squares denote the broad feature centered near ~ 340 cm^{-1} observed at low pressure in $Pm\bar{3}m$ phase.

disorder-induced Raman scattering, where local structural distortions partially relax the symmetry selection rules in the nominally cubic phase [4]. In addition, the surface oxidation in powdered samples could be another factor that leads to the broad peak [18].

Upon increasing pressure to 2.6 GPa, where the sample's structure transforms from $Pm\bar{3}m$ to $Im\bar{3}$ phase, we observe much more uniform reddish color and additional low-frequency Raman modes (A_{1g} and $1E_g$) become discernible, as shown in Fig. 5(a). These two modes in $Im\bar{3}$ phase have been shown to reflect the rotational/tilting motions of nearly rigid ReO_6 octahedra. They harden rapidly with pressure below ~ 5 GPa and continue to shift upward more gradually at higher pressures, reflecting progressive stiffening of the octahedral rotational degrees of freedom [4]. In our Raman spectra, the corresponding low-frequency features also shift to higher frequencies in the $Im\bar{3}$ phase, in a similar manner, as shown in Fig. 5(b).

Upon further compression into the $Im\bar{3}/R\bar{3}c$ coexistence region (~ 9.8 GPa), these modes split and reorganize, coinciding with the pressure range where our PXRD data indicate the emergence of the rhombohedral phase. Since the $R\bar{3}c$ structure is generated by cooperative rotations of the ReO_6 octahedra, the splitting and reorganization of these low-frequency Raman features upon entering the $Im\bar{3}/R\bar{3}c$ coexistence region are consistent with a symmetry-lowering reconstruction of the rotated ReO_6 framework. It is noteworthy that this peak splitting was also reported by I. Efthimiopoulos et al. and was attributed to a possible solidification of PTM (4:1 methanol-ethanol mixture) [4]. We used NaCl as the PTM for Raman measurements, which is not expected to have abrupt changes near ~ 10 GPa, so we attribute the observed splitting primarily to the intrinsic structural evolution and/or phase coexistence.

To further assess the lattice response associated with this structural evolution, we analyzed the pressure-dependent unit-cell volume using Birch–Murnaghan equation-of-state fits for the single-phase $Im\bar{3}$ and $R\bar{3}c$ regions (Fig. s2). Both PXRD runs yield a smaller fitted bulk modulus B_0

for the higher-pressure $R\bar{3}c$ phase than for the lower-pressure $Im\bar{3}$ phase, suggesting enhanced compressibility of the rhombohedral phase. Based on these phase-specific bulk moduli and the pressure-dependent Raman mode frequency, a semi-quantitative mode Grüneisen-parameter analysis suggests enhanced compression sensitivity of the low-frequency A_g and E_g modes in the $R\bar{3}c$ phase, as discussed in the Supplementary Information.

Above 9.8 GPa, the optical contrast of the sample darkens progressively with increasing pressure and appears nearly black by ~ 28 GPa. Although a faint residual reddish contrast may still be discerned at ~ 26.5 GPa, the Raman spectra at this pressure already display two dominant phonon modes consistent with the rhombohedral $R\bar{3}c$ framework. Group-theoretical analysis for $R\bar{3}c$ symmetry allows four Raman-active modes ($A_g + 3E_g$). In many $R\bar{3}c/R\bar{3}c$ -type oxides, the A_g mode is typically the most intense, whereas the E_g modes are weaker and often partially overlapping. Consistent with this intensity hierarchy, the stronger band observed here is plausibly assigned to the $1A_g$ mode, while the lower-intensity band on its lower-frequency side can be attributed to one of the E_g components. The remaining symmetry-allowed E_g modes may not be individually resolved in our loading. Analogously to distorted variant of cubic ReO_3 structure: TeO_3 [19], one E_g mode may lie close in frequency to $1A_g$ and merge into a single broadened feature due to systematic linewidth broadening. Another E_g mode may shift toward higher frequencies with compression and extend beyond our current spectral window (~ 700 cm^{-1}), rendering it experimentally inaccessible.

Upon further compression to 47.1 GPa, where PXRD results suggest the possible emergence of a high-pressure $R32$ or $P2_1/c$ phase, the Raman response changes qualitatively: the higher-frequency $1A$ -related feature becomes strongly suppressed, replaced by two discernible weak features, located near ~ 600 cm^{-1} , whereas the lower-frequency region evolves into a broadened bump with possible multi-subcomponents, as shown in Fig. 5(a). Given the absence of inversion symmetry in the $R32$ or $P2_1/c$ structure and the systematic linewidth broadening inherent to DAC powder measurements, a definitive mode assignment is not attempted here. A more detailed vibrational characterization of this phase would require measurements under improved hydrostatic conditions and, ideally, polarization-resolved Raman studies on single crystals.

Electrical resistance measurements under pressure, shown in Fig. 6(a–c) and Figs. s7(a–c), reveal a pronounced evolution of the normal-state transport properties of ReO_3 . At low pressure, below 5.5 GPa, the resistance exhibits a typical metallic temperature dependence with a relatively small residual resistance, which decreases with pressure. Upon increasing pressure above approximately 5.5 GPa, the overall magnitude of resistance increases systematically over the entire measured temperature range, indicating a significant modification of the electronic transport upon compression (as shown for 250 K in Fig. 1). This resistance enhancement persists to the highest pressures measured up to ~ 80 GPa, as shown in Fig. 1 and s7. Remarkably, a low-temperature sharp drop in resistance is observed starting at 5.5 GPa and becoming clearer above 9.8 GPa, signaling the onset of SC. The maximum T_c (onset) reaches 17.5 K at 28 GPa. Alternatively, the maximum T_c is 14 K at 22 GPa, as shown in Fig. 6(b), if the 50% criterion for T_c is used. The normal-state resistance above the transition remains comparatively large, indicating that the emergence of SC in compressed ReO_3 is not associated with a reduction of the normal-state resistance. The width of the resistive signature associated with T_c above 36 GPa becomes much broader and the loss of zero resistance above 50 GPa suggests the gradual loss of the bulk nature of the SC and/or the enlargement of the pressure gradient.

To further confirm and characterize the SC phase, we measured $R(T)$ under different magnetic fields. A representative dataset recorded at 28.0 GPa is shown in Fig. 6(g). As the magnetic field is increased, the SC transition is progressively suppressed, providing further confirmation that the transition in resistance is consistent with the onset of SC. The

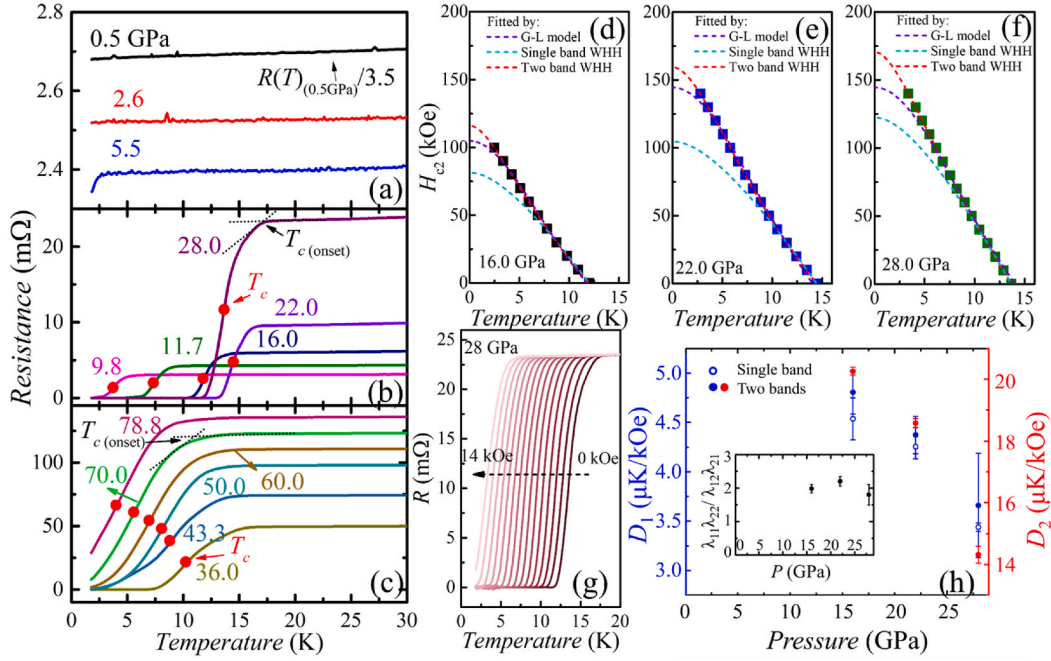


Fig. 6. Superconductivity properties of powder ReO3 under pressure (a)–(c) Temperature dependence of the electrical resistance $R(T)$ in the low-temperature range at selected pressures from 0.5 to 78.8 GPa, illustrating the evolution of the superconducting transition under compression. The criterion for defining the superconducting transition temperature T_c is the midpoint of the superconducting transition [red symbols in panels (b) and (c)]. Whereas, $T_{c,onset}$ is determined from the intersection of two extrapolated dashed lines drawn along the normal-state and transition-region slopes, as shown in panel (b). (d)–(f) Upper critical field $\mu_0 H_{c2}$ as a function of temperature at $P = 16.0, 22.0$, and 28.0 GPa, respectively. H_{c2} (T) values are determined from 50% resistance criterion relative to the normal-state resistance. (g) $R(T)$ at different magnetic fields at 28.0 GPa. (h) The pressure-dependent fitting parameters obtained from the two-band WHH model.

transition width does not show substantial additional broadening under magnetic field, and similar behavior is observed at 16.0 GPa and 22.0 GPa (Fig. s7). This behavior indicates that the SC component contributing to the resistive transition has a relatively well-defined field scale, without a broad distribution of local T_c or H_{c2} values and with the irreversibility field being very close to the H_{c2} . However, this should not be interpreted as evidence that the entire sample is structurally homogeneous at all pressures. In particular, 16.0 GPa lies close to the $Im3/R3c$ coexistence regime according to the room temperature PXRD results shown in Fig. 2. In addition, the use of solid NaCl as the PTM in the transport measurements may create a different local pressure environment from that in the PXRD measurements, leading to possible differences in the nominal pressure scale and phase-coexistence range.

We also plot the temperature at which the resistance drops by 50% from the normal-state value under various magnetic fields at different pressures ($16, 22$, and 28 GPa) and fit the data using Ginzburg-Landau (G-L) [20], single band [21], and double band Werthamer-Helfand-Hohenberg (WHH) [22].

The G-L model follows the expression:

$$H_{c2}(T) = \frac{H_{c2}(0)(1 - t^2)}{1 + t^2} \quad (1)$$

where $t = T/T_c$. The single band WHH model follows the equation:

$$H_{c2} = \frac{2\pi k_B T}{D_1 e} \left[1 - 2\psi^{-1} \left[\ln \frac{T}{T_c} - \psi \left(\frac{1}{2} \right) \right] \right] \quad (2)$$

where ψ is the digamma function, and the band diffusivity $D_1 \propto \frac{\partial H_{c2}}{\partial T} \big|_{T_c}$ is the only fitting parameter. The two-band model in which H_{c2} and T are related by the following equation:

$$\begin{aligned} & a_0 \left[\ln \frac{T}{T_c} + \psi \left(\frac{1}{2} + \frac{D_1 e H_{c2}}{2\pi k_B T} \right) \right] \left[\ln \frac{T}{T_c} + \psi \left(\frac{1}{2} + \frac{D_2 e H_{c2}}{2\pi k_B T} \right) \right] \\ & + (1 + \lambda_-) \left[\ln \frac{T}{T_c} + \psi \left(\frac{1}{2} + \frac{D_1 e H_{c2}}{2\pi k_B T} \right) \right] \\ & + (1 - \lambda_-) \left[\ln \frac{T}{T_c} + \psi \left(\frac{1}{2} + \frac{D_2 e H_{c2}}{2\pi k_B T} \right) \right] = 0 \end{aligned} \quad (3)$$

where $a_0 = 2 \frac{\lambda_{11}\lambda_{22} - \lambda_{12}\lambda_{21}}{\sqrt{\lambda_+^2 + 4\lambda_{12}\lambda_{21}}}$, $\lambda_- = \lambda_{11} - \lambda_{22}$, and λ_{ij} are the intraband ($i = j$) and interband ($i \neq j$) scattering coefficients. For the case where the intraband scattering of both bands is similar, $\lambda_- \approx 0$ and $a_0 \approx \frac{\lambda_{11}\lambda_{22}}{\lambda_{12}\lambda_{21}} - 1$.

The fitting curves corresponding to the three models described above are shown in Fig. 6(d–f). Whereas the GL model describes the $H_{c2}(T)$ data well in the vicinity of T_c , a clear deviation emerges at low temperatures, where the experimental data points exceed the GL extrapolation and display a slight upward curvature. On the other hand, the single-band WHH model also fails to capture the low-temperature enhancement of H_{c2} observed in our data. And in fact, the deviation at low temperatures is more pronounced than that obtained from the fit to the GL model. This indicates that the breakdown of the single-band description is intrinsic. Thus, we performed a two-bands WHH fit. In this case, the data at all three pressures can be well fitted using only three parameters: D_1 , D_2 and a_0 . The obtained parameters are plotted in Fig. 6(h). Within the two-band WHH analysis, both band diffusivities decrease monotonically with pressure from 16 to 28 GPa, with D_1 reduced from 4.8 to 3.8 $\mu\text{K}/\text{kOe}$ and D_2 from 20 to 14 $\mu\text{K}/\text{kOe}$. Importantly, the diffusivity ratio remains nearly constant, indicating that the pronounced two-band asymmetry persists throughout this pressure range rather than evolving toward a single-band limit. In the dirty-limit picture D_i is proportional to the Fermi-surface average of $v_{F,i}^2 \tau_i$. The simultaneous suppression of D_1 and D_2 implies an overall reduction of the effective quasiparticle diffusivity under compression, consistent with the resistance increase under pressure. The fact that D_1 remains

substantially smaller than D_2 further suggests that the low-temperature/high-field scale of H_{c2} continues to be governed primarily by the slower (more diffusive-limited) band, while the faster band mainly shapes the curvature of $H_{c2}(T)$ near T_c .

The magnetic susceptibility measurements shown in Fig. 7(a) were performed at pressures from 7.8 to 37 GPa as a function of temperature under an applied magnetic field of 0.2 kOe. A pronounced diamagnetic transition first becomes observable at 10.7 GPa, with an onset T_c of ~ 10 K and a shielding volume fraction below 20% at 5 K. In all cases, the diamagnetic transition is not complete at 5 K, so that the estimation of the shielding volume fraction at 5 K should be regarded as an underestimate, in particular for lower T_c values. Upon increasing pressure from 10.7 to 29.4 GPa, both the onset T_c and the shielding volume fraction systematically increase, reaching a maximum shielding fraction of about 60% at 5 K at 29.4 GPa, indicative of the emergence of bulk SC. Further compression leads to a gradual suppression of SC, with both the onset T_c and the shielding volume fraction decreasing to below 20% at 5 K at 37 GPa.

In addition to conventional magnetization measurements under finite magnetic fields, trapped-flux measurements were performed to further verify the bulk nature of SC in ReO_3 . As shown in Fig. 7(b), a clear SC transition is observed in the trapped-flux magnetic moment, which vanishes upon warming above T_c . Both the trapped-flux signal amplitude and T_c exhibit pressure dependences consistent with the field-dependent susceptibility data in Fig. 7(a). This behavior arises from irreversible magnetic flux trapping due to vortex pinning in the SC state, leading to a persistent magnetic signal in zero applied field that cannot be accounted for by surface/filamentary SC. In addition, the observation of a trapped-flux signal provides strong complementary evidence for bulk SC [23,24]. The irreversible trapping of flux is a direct signature of

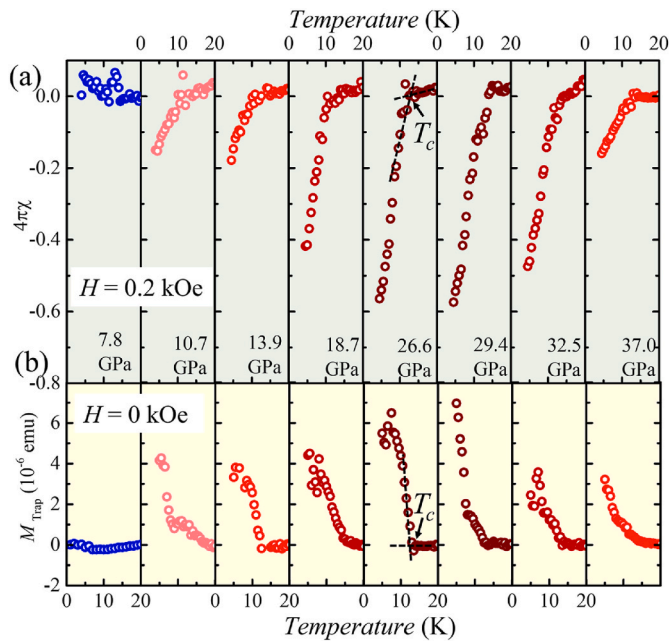


Fig. 7. Magnetic susceptibility and trapped flux magnetization of ReO_3 under pressure. (a) Zero-field-cooled temperature dependent magnetic susceptibility at various pressures, with the external field $H = 0.2$ kOe perpendicular to the disk-like polycrystalline sample. (b) Temperature dependent trapped flux magnetization at various pressures. The trapped flux measurements were performed by cooling the DAC from 50 to 5 K in an external field, $H = 20$ kOe perpendicular to the disk-like polycrystalline sample, stabilizing the temperature at 5 K for 10 min, and then removing the field. The magnetization was then measured upon warming from 5 to 20 K. The criteria for defining T_c used here are the intersection of two extended dashed lines along the $M(T)$ and $M_{\text{trap}}(T)$ curve above and below the transition temperatures, shown in the curves of 26.6 GPa.

vortex pinning within the bulk SC volume, confirming the intrinsic bulk nature of the SC state in ReO_3 over the 20–32 GPa pressure range.

ReO_3 at ambient pressure exhibits a pronounced NTE below ~ 200 K, driven by thermally activated rotations (tilts) of its corner-sharing ReO_6 octahedra [3]. Under higher pressures, as shown in Fig. 8(a), this unusual NTE behavior persists, but its onset shifts to relatively lower temperature, and the magnitude of the lattice volume contraction is much more enhanced than at ambient pressure.

It should be noted, though, that at high pressures the PXRD patterns (performed at beamline 3-ID-B, Advanced Photon Source, Argonne National Laboratory, which has very small spot size $\sim 5 \times 5 \mu\text{m}^2$) exhibit pronounced azimuthal intensity inhomogeneity, manifested as spotty or segmented rings rather than uniform powder rings. This behavior primarily reflects incomplete powder averaging with much small beam size used in the DAC, where the reduced illuminated volume limits the number of randomly oriented crystallites contributing to each reflection and enhances grain-statistics effects. Nonhydrostatic stress components due to the solidification of the PTM (neon) at high pressure may also introduce micro-strain and partial crystallite reorientation, amplifying intensity variations along the rings. Here, we adopted two approaches to extract reliable lattice parameters. First, Le Bail fits were performed using a two-phase model ($\text{ReO}_3 + \text{Neon}$), which refines peak positions and profiles without relying on intensity constraints. Second, lattice parameters were independently determined by directly indexing selected isolated ReO_3 reflections, as shown in Fig. 8(a).

At 25 GPa and 30 GPa, where bulk SC is well established and the $R\bar{3}c$ phase is dominant, both lattice-parameter extraction procedures reveal a similar downturn of the unit-cell volume upon cooling below approximately 35 K. The pressure, monitored by ruby fluorescence at each temperature, remains relatively constant in this low-temperature range, as shown in Fig. 8(b), indicating that the anomaly is not simply caused by pressure drift. A comparably clear anomaly is not resolved in the

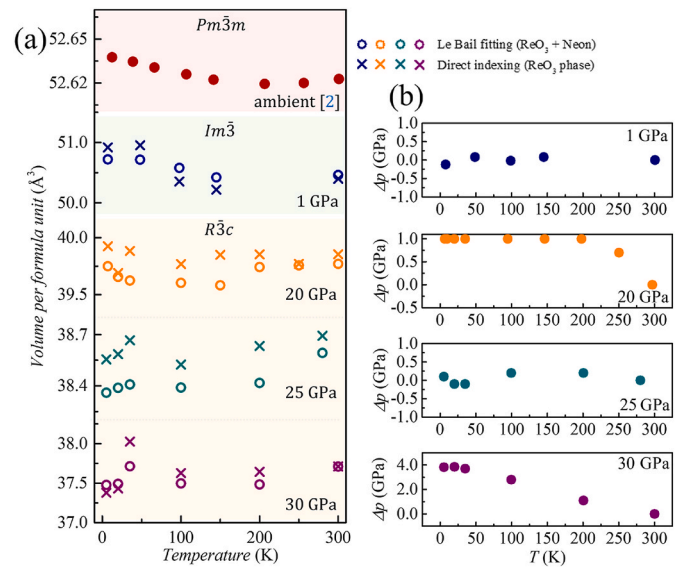


Fig. 8. Low-temperature behavior of the unit cell volume at various pressures. (a) Temperature dependence of the volume per formula unit at selected pressures. Red solid circles denote the ambient-pressure data digitized from Ref. [2]. Hollow circles represent lattice parameters obtained from Le Bail refinement (including ReO_3 and Ne phases), whereas crosses correspond to volumes extracted from direct indexing of selected reflections in the PXRD patterns (see Fig. S8 for detailed data). The weighted profile factors of the Le Bail fits are in the range $R_w = 3$ –12%, indicating reasonable refinement quality under high-pressure DAC conditions. (b) Temperature dependence of the relative pressure change, $\Delta p = p - p_{\text{max}} T$, determined from ruby fluorescence measurements at selected pressures, allowing evaluation of possible pressure drift upon cooling.

20 GPa dataset. However, this absence should be interpreted with caution. The phase boundaries of ReO_3 depend on the PTM and experimental conditions: whereas the first room-temperature PXRD run (run 1, Fig. 2) using 4:1 methanol-ethanol identifies the $R3c$ -dominant region above approximately 20 GPa, the second PXRD run (run 2, Fig. s1) using neon shows that the $Im3/R3c$ coexistence region can extend to nearly 26 GPa. Since the low-temperature PXRD measurements were also performed using neon as the PTM, the condition at 20 GPa may still be in the $Im3/R3c$ coexistence region. Under such circumstances, local stress between coexisting phase-domains and pressure gradient could mask a subtle intrinsic lattice response of the $R3c$ phase. Moreover, the low-temperature PXRD measurements have more limited low-angle coverage than room-temperature measurements, where several reflections diagnostic of phase coexistence are expected. Thus, the lack of a clear volume anomaly at nominal 20 GPa does not necessarily rule out its association with the more fully developed $R3c$ SC regime. Meanwhile, the temperature sampling in the current dataset is relatively sparse, particularly in the 5–50 K range. Clarifying the relationship between SC and this lattice anomaly will require additional high-resolution low-temperature structural studies, ideally performed under identical PTM conditions and with improved low-angle coverage, to determine the microscopic origin and physical significance of the anomaly.

3. Conclusions

In summary, our comprehensive high-pressure study of ReO_3 establishes a close relation between lattice symmetry, electron-phonon coupling, and the emergence and suppression of bulk superconductivity (SC). Bulk SC with the maximum onset $T_c \sim 17.5$ K emerges exclusively within the rhombohedral $R3c$ phase, where cooperative ReO_6 octahedral rotations reconstruct the oxygen framework and create a favorable environment for strong electron-phonon coupling (EPC). The calculations reveal that the enhanced EPC arises from cooperative Re-O lattice dynamics, with substantial contributions from both low-frequency Re-associated modes and higher-frequency O-associated modes. Upon further compression, both experiment and theoretical calculation reveal an instability of the rhombohedral SC phase toward reconstructed lower-symmetry states associated with significant electronic reconstruction. Whereas the high-pressure diffraction patterns can be best fitted with an $R32$ -like average distortion that nearly doubles the unit cell, theoretical calculations instead predict a competing $mP16-P2/c$ structure driven by phonon instability and increased Re-O coordination. Importantly, this denser higher-coordination phase suppresses the SC by reducing the density of states at the Fermi level and weakening the overall EPC. In addition, we uncover robust NTE across multiple pressure-stabilized phases and identify a curious low-temperature volume anomaly below 35 K that is probably related to the SC regime, potentially signaling enhanced lattice instability in proximity to the high-pressure symmetry-breaking transition. These results demonstrate that SC in compressed ReO_3 is governed not simply by pressure-induced densification, but by a delicate balance between oxygen-framework geometry, electronic structure, and phonon-mediated pairing in a simple 5d oxide.

4. Methods

4.1. Sample acquisition and preparation

Rhenium (VI) oxide (ReO_3) powder (CAS No. 1314-28-9) with 99.9% (metals basis) purity was purchased from Thermo Scientific Chemicals. To preserve sample quality, the powder container was opened and stored exclusively in an Ar-filled glovebox. Since ReO_3 thermally

decomposes above approximately 400 °C, the small amount of powder taken for synchrotron experiments was placed in a small jar under Ar atmosphere. The jar lid was sealed with airtight membrane tape to maintain an inert environment, avoiding vacuum sealing in silica tubes that requires flame-heating and could potentially cause slight decomposition or oxygen loss during the sealing process. All experiments were conducted using the as-received powder without further purification.

4.2. Electrical transport under high pressure, optical micrograph and low frequency Raman spectra

Electrical resistance was measured up to 80 GPa using a CuBe diamond-anvil pressure cell (DAC) (Bjcsistar) compatible with a Quantum Design Physical Property Measurement System (PPMS) [25]. The cell employed Type Ia diamond anvils with 200 μm culet size and a stainless-steel gasket. After pre-indenting the gasket to ~ 15 GPa, a concentric 200 μm hole was drilled by electric-discharge machining (EDM) and back-filled with a cured mixture of cubic BN powder and epoxy. This insert was then compressed to 15 GPa again and re-drilled using a mechanical drilling machine to a 100 μm diameter hole to form the sample chamber.

The bottom space of the sample chamber was first covered with a thin NaCl layer along with a small ruby sphere. ReO_3 powder was placed above this layer, and the Pt foil electrodes were arranged in a van der Pauw configuration on the pressed powder sample. An additional thin NaCl layer was placed over the sample and electrodes to improve the hydrostaticity at high pressure. Schematics of the sample chamber at various pressures are shown in Fig. s6. Pressure was determined from the ruby $R1$ fluorescence line below 50 GPa and from the first-order diamond Raman edge above 50 GPa [26,27]. It is noteworthy that several pressure points between 30 and 50 GPa were calibrated using both the ruby fluorescence line and the diamond Raman edge, confirming the consistency between these two pressure gauges.

All pressures assigned to the transport data were determined at room temperature. In an auxiliary calibration (shown in Fig. s9) test using the same DAC configuration and an initial pressure of approximately 8.0 GPa an appreciable increase in the sample-chamber pressure was observed upon cooling using ruby fluorescence measurements. Because this pressure drift depends on the initial pressure and cooling protocol, no numerical correction was applied to the transport data.

Optical micrographs were recorded at each pressure using a CCD camera. For consistency, the brightness of all images was adjusted by normalizing to the intensity of the Pt wires, which serve as an internal reference. This procedure ensures that relative changes in the apparent color of the sample can be directly compared across different pressures.

Low-frequency Raman scattering measurements were performed using a Raman spectrometer (Horiba IHR-550) with a laser excitation wavelength of 633 nm. A $50\times$ objective lens was used to focus the incident laser beam, and all spectra at different pressures were collected from the same position near the center of the sample.

4.3. Magnetization under high pressure

DC magnetization measurements were performed in a Quantum Design Magnetic Property Measurement System (MPMS) down to 5 K using an easyLab Mcell Ultra DAC [28] equipped with 400 μm culet anvils. An apertured tungsten gasket with a 200 μm hole served as the sample chamber. Nujol mineral oil served as the pressure-transmitting medium (PTM) [29]. Pressure was measured by the ruby fluorescence $R1$ line [26,27].

Background signals of the empty DAC (the DAC was closed with all parts except for the sample) were measured at 4.4 GPa in an applied field of 0.2 kOe for magnetic susceptibility $M(T)$. The trapped-flux magnetization, $M_{\text{trap}}(T)$, of the background was also measured: the empty DAC was cooled from 30 K to 5 K in a 20 kOe external magnetic field, stabilized at 5 K for 10 min, the field was then removed, and M_{trap} .

background(T) was recorded while warming from 5 K to 30 K with a 0.5 K step size. The temperature was stabilized at each step for 40 s.

It is noteworthy that the magnetization measurements were carried out on a pressed powder sample of ReO_3 rather than on a bulk single crystal. Accordingly, corrections associated with the sample density and demagnetization effects were taken into account when estimating the volume shielding fraction. The pressed powder pellet was prepared in an Ar-filled glovebox using a hydraulic press with a load of 3000 lbs. The resulting pellet density was estimated to be approximately 3.67 g/cm^3 , corresponding to about 53% of the nominal density of ReO_3 (6.92 g/cm^3), which yields a susceptibility correction factor of $f \approx 1/0.53 \approx 1.9$. A thin rectangular piece with dimensions of $\sim 120 \mu\text{m} \times 100 \mu\text{m} \times 20 \mu\text{m}$ was cut from the pellet and loaded into the DAC, resulting in an estimated demagnetization factor of $n \approx 0.8$ [30]. After background acquisition, the DAC was opened, the ReO_3 piece was loaded into the sample chamber, and the same measurement protocols were repeated at various pressures. Sample magnetization was obtained by point-by-point subtraction of long-scan responses with and without the sample, followed by dipole fitting of the subtracted scan [31].

4.4. Synchrotron powder X-ray diffraction

Room-temperature high-pressure powder X-ray diffraction (PXRD) measurements were performed at beamline 13-BM-C (GSECARS), Advanced Photon Source, Argonne National Laboratory. Monochromatic X-rays with a wavelength of $0.4306 \text{ \AA}$ were focused to a $10 \mu\text{m} \times 10 \mu\text{m}$ spot. Fresh ReO_3 powder, protected under an argon atmosphere, was rapidly loaded into a wide-opening BX-90 DAC [32] equipped with type Ia diamonds with $300 \mu\text{m}$ culets, a pre-indented Re gasket, and two ruby spheres ($<10 \mu\text{m}$ in diameter) for pressure calibration. A methanol:ethanol (4:1) mixture was used as the PTM for run 1, while neon was employed for run 2.

Low-temperature high-pressure PXRD experiments were conducted at beamline 3-ID-B, Advanced Photon Source, Argonne National Laboratory. X-rays with a wavelength of $0.4875 \text{ \AA}$ were focused to a $5 \mu\text{m} \times 5 \mu\text{m}$ spot. An iBX80 DAC equipped with $500 \mu\text{m}$ culet size conical anvils providing an 80° optical opening angle, was used for applying pressure. Low-temperature conditions were achieved using a Lake Shore Model RGC4 cryogen-free closed-cycle refrigeration system and a DaTools custom cryostat. Pressure was controlled in situ using a double-sided gas-membrane system. Temperature-dependent PXRD measurements at each pressure point were conducted independently. Pressure was first stabilized at 300 K (280 K for 25 GPa). The sample was subsequently cooled to the desired temperature, followed by a waiting time of $\sim 20 \text{ min}$ for the temperature stabilization prior to diffraction data acquisition. Pressure was monitored at each temperature point. Pressure for all measurements was determined in situ from the calibrated shift of the ruby R1 fluorescence line [26,27]. Two-dimensional diffraction images were integrated using DIOPTAS [33], symmetry indexing, and Rietveld/Le Bail refinements were carried out with GSAS-II [34].

4.5. Computational methods

Electronic structure and total energy calculations in density functional theory [35,36] (DFT) have been performed with PBE [37] exchange-correlation functional using a plane-wave basis set and projector augmented wave method [38], as implemented in the Vienna Ab-initio Simulation Package [39,40] (VASP). We use a kinetic energy cutoff of 500 eV, Γ -centered Monkhorst-Pack [41] k -meshes with a reciprocal density of $0.025 (1/\text{\AA}^3)$, and a Gaussian smearing of 0.05 eV. For enthalpy calculations of ReO_3 in different crystal structures, the shape of the unit cells and ionic positions are relaxed until the absolute value of force on each atom is less than $0.01 \text{ eV/\AA}$ for the volumes scaled around the equilibrium. Then these results are fit to Birch-Murnaghan [42] equation of state to evaluate pressure and enthalpy. The phonon

and electron-phonon coupling (EPC) spectra are calculated in density functional perturbation theory [43] as implemented in Quantum ESPRESSO [44] (QE) using ultrasoft pseudopotentials [45,46] with a kinetic energy cutoff of 50 Ry and a Gaussian smearing of 0.02 Ry. Spin-orbit coupling (SOC) was not included in the Quantum ESPRESSO EPC calculations. The phonon-mediated SC properties have been calculated in the isotropic Eliashberg approximation with the SC critical temperature (T_c) estimated in McMillan-Allen-Dynes formula [47] with a Coulomb potential of 0.16. The workflows of these first-principles calculations have been streamlined in our recently developed high-throughput electronic structure package [48–51] (HTESP).

CRediT authorship contribution statement

S. Huyan: Writing – review & editing, Writing – original draft, Visualization, Project administration, Methodology, Formal analysis, Data curation, Conceptualization. **R.F.S. Penacchio:** Writing – review & editing, Writing – original draft, Visualization, Formal analysis, Data curation. **L.-L. Wang:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Investigation, Formal analysis, Data curation. **J. Schmidt:** Writing – review & editing, Visualization, Formal analysis, Data curation. **D. Zhang:** Writing – review & editing, Formal analysis, Data curation. **B. Lavina:** Writing – review & editing, Formal analysis, Data curation. **Z. Li:** Writing – review & editing, Formal analysis. **R.A. Ribeiro:** Writing – review & editing, Resources, Formal analysis. **T.J. Slade:** Writing – review & editing, Formal analysis. **J. Zhao:** Writing – review & editing, Formal analysis, Data curation. **S.L. Morelhão:** Writing – review & editing, Formal analysis. **P. C. Canfield:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization. **S.L. Bud'ko:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mtphys.2026.102206>.

Data availability

Data will be made available on request.

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