

High-pressure synthesis of an arsenopyrite-type polymorph of ReS_2 recoverable to ambient conditions

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(Received 18 November 2025; accepted 11 March 2026; published 30 March 2026)

Transition-metal dichalcogenides have attracted a great deal of attention in the context of two-dimensional materials because of their electronic properties, derived from their layered crystal structures, as well as their exfoliability. Surprisingly, the combination of high pressure and high temperature has been rarely exploited in the study of these systems, although it is expected to be an efficient way of inducing the formation of novel polymorphs. Here, rhenium and carbon disulfide were observed to react at a pressure of 54 GPa in a laser-heated diamond anvil cell to form a hitherto unknown polymorph of rhenium disulfide, denoted as $mP12\text{-ReS}_2$ in the Pearson notation. Its crystal structure was solved and refined using synchrotron single-crystal x-ray diffraction data, revealing that $mP12\text{-ReS}_2$ adopts the arsenopyrite structure type (space group $P2_1/c$). The structure is characterized by an extended three-dimensional framework of corner- and edge-sharing distorted ReS_6 octahedra. Raman spectroscopy data further confirm the formation and structure of $mP12\text{-ReS}_2$. Remarkably, upon decompression, $mP12\text{-ReS}_2$ was recovered to ambient conditions and found to be stable in air. Thermodynamic, electronic, and bonding properties of the new phase were also studied computationally within the framework of density functional theory. From these, $mP12\text{-ReS}_2$ is found to be semimetallic at 0 GPa, and to have a lower enthalpy than the previously known ReS_2 polymorph from ~ 0.5 GPa onwards. The discovery of this new compound warrants further investigations of its physical properties, and may open new possibilities for applications.

DOI: [10.1103/4wwn-75qm](https://doi.org/10.1103/4wwn-75qm)

I. INTRODUCTION

Transition-metal dichalcogenides (TMDs), with the general formula TX_2 , where T denotes a transition metal atom and X represents S, Se, or Te, are an established class of materials with many useful properties. They have recently gained significant attention, particularly in the context of two-dimensional materials [1,2]. Their structural building blocks are trigonal prismatic, octahedral, or distorted octahedral polyhedra, each with the T atom as the coordination center. For many TMDs, the stacking of these blocks results in structures characterized by layered (i.e., laminar) arrangements [3,4]. These laminar TMDs, in which the layers are held together by weak van der Waals interactions, can be readily exfoliated into monolayers [2,5]. Remarkably, some of them undergo a transition from indirect to direct band gap semiconductors when reduced from bulk to monolayer form [6,7]. Moreover, TMDs exhibit a variety of electronic properties, spanning the full spectrum from insulators (e.g., HfS_2) to semiconductors (e.g., MoS_2), metals (e.g., VSe_2), and superconductors (e.g., NbSe_2). Among

their other exceptional properties, TMDs feature strong light-matter interactions, high carrier mobility, and mechanical flexibility, making them highly suitable for next-generation applications in electronics and optoelectronics [1,7].

On account of their attractive nature, there is great interest in investigating the behavior of TMDs as a function of external parameters such as temperature, pressure, electrostatic doping, electric and magnetic field, and strain [2,3,5,8–11], in part as an attempt to manipulate their physical properties. Surprisingly, the combination of high pressure and high temperature has thus far been significantly underexploited in the study of these systems, although it is well established to be an extremely efficient way of tuning crystal structures and electronic properties, as well as inducing the formation of novel thermodynamically stable compounds. In studies involving only the application of high pressure to TMDs, lattice distortions, interlayer coupling, phase transitions, charge-density wave suppression, metallization, and superconductivity have been reported [12–27].

ReS_2 , which is found in nature as the mineral rheniite, crystallizes in a distorted CdCl_2 -type structure with space group $P\bar{1}$ (No. 2) and contains 12 atoms per unit cell [28,29]. This compound, labeled as $aP12\text{-ReS}_2$ in the Pearson notation, is composed of edge-sharing distorted ReS_6 octahedra that assemble in two-dimensional layers. It is a direct band gap semiconductor at ambient pressure, with a gap of ~ 1.4 eV. Previous high-pressure investigations of ReS_2 reported a phase transition occurring between 2.5 and 11 GPa [30–35].

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Although the structure of the resulting phase could not be unambiguously solved, more than one study suggested that it retains the triclinic $P\bar{1}$ space group [30–33]. Also, upon further compression to pressures between ~ 27.5 and ~ 38.5 GPa, metallization has been reported to occur [30,31]. Interestingly, computational studies [36,37] have predicted high-pressure phases of ReS_2 with lower enthalpy than the known polymorph, but these have not been experimentally observed. Given the often-stifling effect of activation barriers in preventing access to thermodynamically stable structures, combining high pressures with high temperatures is vital to test these predictions. To the best of our knowledge, such experiments have not yet been attempted on ReS_2 .

Here, we report the high-pressure, high-temperature synthesis of a hitherto unknown polymorph of ReS_2 , $mP12\text{-ReS}_2$. This phase was formed at 54 GPa following the laser-heating of CS_2 and a Re gasket in a diamond anvil cell (DAC). The structure of the new phase was characterized by means of synchrotron single-crystal x-ray diffraction (SCXRD) and is found to be comprised of a three-dimensional framework of corner- and edge-sharing ReS_6 octahedra. Complementary high-pressure Raman spectroscopy data were also collected. The sample was then decompressed in a few steps down to ambient pressure, with SCXRD data collected at each step. Remarkably, this novel polymorph of ReS_2 was found to be recoverable at ambient pressure and temperature, as well as stable in air. Density functional theory (DFT) calculations were performed over the pressure range of 0 to 60 GPa to assess the thermodynamic, electronic, and bonding properties of the new solid.

II. METHODS

A. Sample preparation

A BX90-type screw-driven DAC [38] equipped with Boehler-Almax type diamonds (culet diameter of 250 μm) was used for these experiments. A 200- μm thick rhenium foil was indented down to 25 μm to be employed as gasket and a sample cavity of 120 μm in diameter was laser-drilled at the center of the indent. The loading of the DAC with liquid carbon disulfide (CS_2 , purity $\geq 99.9\%$, Sigma Aldrich) was performed at room temperature under a fume hood. Note that CS_2 is highly flammable and toxic; special care is needed during handling. The sample was compressed to 54 GPa and laser-heated to temperatures above 1500 K using a custom-built Nd:YAG laser setup ($\lambda = 1064$ nm) at the European Synchrotron Radiation Facility (ESRF; Grenoble, France). The laser-beam spot was about 15 μm in diameter. Both the Re and CS_2 solids coupled with the laser, CS_2 being black (and amorphous) above about 8 GPa [39]. It can also be noted that 1500 K is above the known decomposition temperature of CS_2 at 54 GPa [40].

B. X-ray diffraction and Raman spectroscopy setups

The XRD measurements at 54 GPa were performed at the ID11 beamline of the ESRF with the x-ray beam ($\lambda = 0.2846$ Å) focused down to 1 $\mu\text{m} \times 1 \mu\text{m}$. Further XRD data were collected at 25 GPa, 7 GPa, and ambient pressure at the P02.2 beamline of Petra III at the Deutsches Elektronen-

Synchrotron (DESY; Hamburg, Germany) with the x-ray beam ($\lambda = 0.2903$ Å) focused down to 2 $\mu\text{m} \times 2 \mu\text{m}$. Pressure was determined from XRD measurements, using the unit cell volume of the unreacted Re and its equation of state [41]. The precision of the pressure measurement is estimated to be of ± 1 GPa. The DAC was fully opened before the final XRD measurement was taken, ensuring that the sample was at ambient pressure and also exposed to air. Raman spectroscopy measurements at 54 GPa were done in a back-scattering geometry using a custom-built microfocused Raman system at the Centre for Science at Extreme Conditions of the University of Edinburgh (UK), which employs a laser with an excitation wavelength of 488 nm. All measurements were performed at room temperature.

C. X-ray diffraction data acquisition and structure determination

Laser-heating at the interface between CS_2 and the Re gasket resulted in the formation of multiple single-crystal grains of the $mP12\text{-ReS}_2$ phase. At each pressure point, an XRD map was collected on the laser-heated area of the sample chamber including the irradiated edge of the gasket. The sample positions displaying the most and the strongest single-crystal reflections belonging to the new phase were chosen for acquisition of single-crystal data, collected in step scans of 0.5° from -36 to $+36^\circ$ —the full angular aperture of our DAC. Exposure time was of 0.3 to 1 s per frame, depending on the dataset. The CrysAlis^{Pro} software package (version 171.43.67) was employed to perform the peak search, indexing, data integration, frame scaling, and absorption correction. The DAFi program [42] was used to identify reflections belonging to distinct grains. In each dataset, many ReS_2 grains were observed, with some of sufficient quality for SCXRD structure determination. Finally, within the Olex2 software [43], the crystal structure was solved using SHELXT [44] and refined using SHELXL [45]. The instrument model used in CrysAlis^{Pro} was calibrated with an orthoenstatite single crystal $[(\text{Mg}_{1.93}\text{Fe}_{0.06})(\text{Si}_{1.93}, \text{Al}_{0.06})\text{O}_6]$, space group $Pbca$, and lattice parameters of $a = 8.8117$ Å, $b = 5.1832$ Å, and $c = 18.2391$ Å; $V = 832.16$ Å³. Crystal structure visualizations were generated using the VESTA software [46].

D. Density functional theory calculations

First-principles calculations were conducted within the framework of DFT using Quantum ESPRESSO [47,48], with optimized norm-conserving Vanderbilt pseudopotentials [49], and the Perdew-Burke-Ernzerhof revised for solids (PBEsol) exchange-correlation functional [50]. A kinetic-energy cutoff of 100 Ry was employed for the plane-waves expansion. For the Brillouin-zone integration of the charge density, a $12 \times 12 \times 12$ Monkhorst-Pack grid with a 0.02 Ry Methfessel-Paxton smearing was employed when $mP12\text{-ReS}_2$ is metallic (0–20 GPa). For pressures at which $mP12\text{-ReS}_2$ is a (very) small band gap semiconductor (30–50 GPa), the electronic bands were calculated employing both smearing and fixed electronic occupations (maintaining the same k grid as before), and found consistent. At 54 GPa and above, only fixed electronic occupations were used. The electronic density of states was obtained by recomputing non-self-consistently the

Kohn-Sham eigenvalues on a $18 \times 18 \times 18$ grid, and integrated using the tetrahedron method. Phonons were computed on a $2 \times 2 \times 2$ grid, and Fourier interpolated to obtain the phonon dispersions and density of states, neglecting all finite-temperature contributions to the lattice dynamics. The Raman/IR activity of the phonon modes was determined based on the symmetry properties of their irreducible representations.

The band gap was also estimated via a direct self-consistent calculation using the Heyd-Scuseria-Ernzerhof screened hybrid functional [51], employing a fraction of exact exchange of 0.25 and a screening parameter of 0.11 bohr^{-1} . The calculations were performed within a fully self-consistent scheme, an 80 Ry plane-wave cutoff for the Kohn-Sham states, and a $4 \times 4 \times 4$ Monkhorst-Pack k -point mesh. The exact-exchange term was evaluated on a $2 \times 2 \times 2$ auxiliary q -point grid and with a 320 Ry cutoff. This was sufficient to converge the band gap to within 100 meV.

III. RESULTS AND DISCUSSION

At 54 GPa, laser-heating solely CS_2 led to its decomposition. As expected, the formation of phase II of pure S, which adopts the tetragonal space group $I4_1/acd$ (No. 142) [52], was observed, while the C atoms are presumed to have formed diamonds. However, when laser heating was applied at the interface between CS_2 and the Re gasket (see optical image of the sample in Fig. S1 of the Supplemental Material [53]), additional diffraction peaks were detected that could not be explained by diamond, sulfur, or rhenium. The high quality of the resulting crystallites enabled full-structure solution and refinement via the collected SCXRD data. An example of reconstructed reciprocal-space precession image is reported in Fig. 1. The newly formed solid was determined to have the ReS_2 stoichiometry, with space group $P2_1/c$ (No. 14) and lattice parameters $a = 5.4640(17) \text{ \AA}$, $b = 5.4699(8) \text{ \AA}$, $c = 5.569(5) \text{ \AA}$, and $\beta = 113.38(6)^\circ$ [$V = 152.77(16) \text{ \AA}^3$] at 54 GPa. Hereafter, it is referred to as $mP12\text{-ReS}_2$, according to the Pearson notation. The crystal structure of $mP12\text{-ReS}_2$ is of arsenopyrite type (FeAsS), a structure type also adopted by binary compounds such as CoSb_2 [54]. Upon sample decompression, the structure was also solved and refined at 25 GPa, 7 GPa, and ambient pressure, with no evidence of a phase transition. At ambient conditions, lattice parameters are $a = 5.8536(12) \text{ \AA}$, $b = 5.818(8) \text{ \AA}$, $c = 5.9145(18) \text{ \AA}$, and $\beta = 112.02(3)^\circ$ [$V = 186.7(3) \text{ \AA}^3$]. Structural data, data collection, and structure refinement details are summarized in Table I. DFT calculations were also performed on $mP12\text{-ReS}_2$ and the relaxed structure models show excellent agreement with the experimental models (Table I). Moreover, calculated phonon band structures at 0 and 54 GPa display no imaginary or soft modes (see Fig. S2 of the Supplemental Material [53]), further demonstrating the solid's dynamical stability.

A. Structure and properties of $mP12\text{-ReS}_2$ at 54 GPa

In the following, the refined crystal structure of $mP12\text{-ReS}_2$ at 54 GPa is described. All three crystallographically distinct atoms (Re1, S1, and S2) occupy the general 4e Wyckoff site, with the rhenium atom coordinated by six sulfur

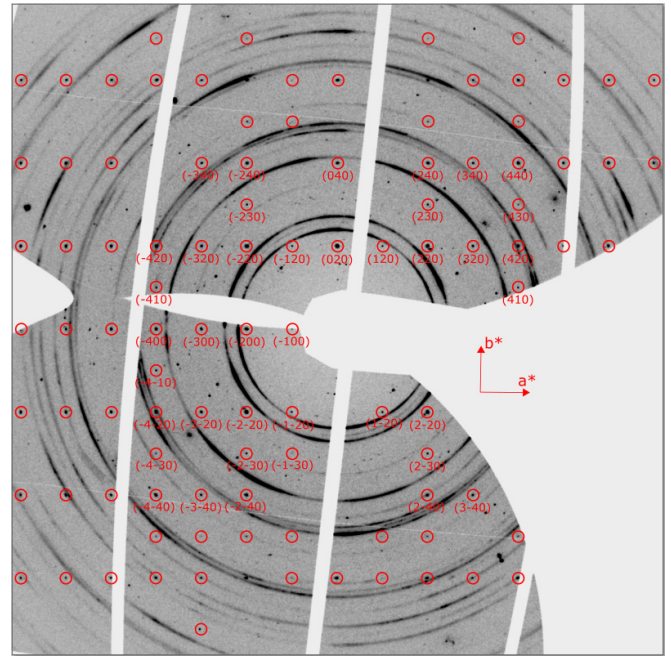


FIG. 1. Reciprocal-space reconstruction image of the $(hk0)$ plane from single-crystal XRD data collected on a $mP12\text{-ReS}_2$ crystallite at 54 GPa. Red circles mark the reflections belonging to the chosen $mP12\text{-ReS}_2$ crystallite, with examples of Miller indices indicated. Signal from unreacted (hcp) Re powder is also visible.

atoms, three S1 and three S2, producing a distorted octahedral geometry. All Re–S distances are unique and fall within the range of $2.184(3)$ to $2.292(6) \text{ \AA}$ [Fig. 2(a)]. The shortest S–S contact is of $2.101(6) \text{ \AA}$, which points to the existence of an S_2 dimer. Indeed, typical bond lengths between S atoms are of $2.0\text{--}2.2 \text{ \AA}$ for single bonds [55]. Given that the measured value lies within this range, the S_2 dimer in $mP12\text{-ReS}_2$ at 54 GPa is expected to have a charge of 2^- in the ionic approximation, henceforth corresponding to a persulfide, $[\text{S}_2]^{2-}$. As such, the charge balance in the solid is of $\text{Re}^{2+}[\text{S}_2]^{2-}$, with $2+$ being a known oxidation state for Re. Persulfides are well known to exist in a variety of binary metal–sulfur compounds, including, for example, MnS_2 , FeS_2 , CoS_2 , and NiS_2 [56]. Together, the ReS_6 octahedra form a three-dimensional framework where they are interconnected through corners and edges [Figs. 2(b), 2(c), 2(d)]. The ReS_6 octahedra are highly asymmetric and share two opposite edges to form single rows running parallel to the $[101]$ crystallographic direction [Fig. 2(b)]. Adjacent octahedra within a row are related to each other by the inversion-symmetry operator, leading to distances between Re atoms alternating between short [$2.689(3) \text{ \AA}$] and long [$3.378(4) \text{ \AA}$], see Fig. S3 of the Supplemental Material [53]. The short Re–Re contact intersects the longest edge of the ReS_6 octahedron [$3.554(10) \text{ \AA}$], whereas the long Re–Re contact crosses its shortest edge [$3.047(9) \text{ \AA}$]. Figure 3(a) reports the calculated electronic band structure and density of states (DOS) of $mP12\text{-ReS}_2$ at 54 GPa. A small but clear indirect band gap is present ($\sim 0.2 \text{ eV}$), and the total DOS vanishes at the Fermi level, indicating a semiconducting state. Overall, bands exhibit only limited dispersion, which results in sharp DOS peaks that are typical of localized states.

TABLE I. Crystal structure, data collection, and refinement details of $mP12$ -ReS₂ at 54 and 0 GPa, compared with the DFT-relaxed models.

	Experimental	DFT-relaxed			
Chemical formula	ReS ₂	ReS ₂	ReS ₂	ReS ₂	ReS ₂
Formula weight M_r	250.32	250.32	250.32	250.32	250.32
CCDC deposition number	2502668	2502672			
Temperature (K)	293(2)	293(2)			
Pressure (GPa)	54(1)	0	54	0	
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	
a (Å)	5.4640(17)	5.8536(12)	5.4292	5.8519	
b (Å)	5.4699(8)	5.818(8)	5.4968	5.7948	
c (Å)	5.569(5)	5.9145(18)	5.5068	5.9166	
β (°)	113.38(6)	112.02(3)	112.21	112.07	
V (Å ³)	152.77(16)	186.7(3)	152.15	185.93	
Z	4	4	4	4	
μ (mm ⁻¹)	7.49	6.46			
$F(000)$	428	428			
Radiation type	synchrotron ($\lambda = 0.2846$ Å)	synchrotron ($\lambda = 0.2903$ Å)			
Diffractionmeter	ID11, ESRF	P02.2, Petra III, DESY			
Crystal size (mm ³)	$0.001 \times 0.001 \times 0.001$	$0.001 \times 0.001 \times 0.001$			
Index ranges	$-8 \leq h \leq 7$ $-8 \leq k \leq 9$ $-4 \leq l \leq 5$	$-8 \leq h \leq 8$ $-2 \leq k \leq 3$ $-8 \leq l \leq 8$			
No. of integrated reflections	717	327			
No. of independent reflections	339	180			
No. of independent reflections [$I > 2\sigma(I)$]	248	123			
R_{int}	0.024	0.025			
$(\sin \theta / \lambda)_{\text{max}}$ (Å ⁻¹)	0.833	0.713			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.024, 0.058, 1.06	0.059, 0.169, 1.04			
No. of refined parameters	28	18			
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	1.44, -2.26	2.88, -3.31			
Experimental 54(1) GPa					
Atom	Wyckoff site	x	y	z	U_{eq} (Å ²)
Re1	$4e$	0.27022(6)	0.50215(7)	0.28617(12)	0.0054(2)
S1	$4e$	0.1590(5)	0.6204(4)	0.8610(9)	0.0069(14)
S2	$4e$	0.3339(5)	0.1276(4)	0.1878(9)	0.0057(13)
Experimental 0 GPa					
Atom	Wyckoff site	x	y	z	U_{eq} or U_{iso} (Å ²)
Re1	$4e$	0.2726(2)	0.5017(10)	0.2880(3)	0.0129(18)
S1	$4e$	0.154(2)	0.630(6)	0.879(2)	0.021(2)
S2	$4e$	0.3462(19)	0.145(6)	0.180(2)	0.018(2)
DFT-relaxed 54 GPa					
Atom	Wyckoff site	x	y	z	
Re1	$4e$	0.2698	0.5024	0.2886	
S1	$4e$	0.1587	0.6220	0.8668	
S2	$4e$	0.3342	0.1293	0.1888	
DFT-relaxed 0 GPa					
Atom	Wyckoff site	x	y	z	
Re1	$4e$	0.2725	0.5010	0.2886	
S1	$4e$	0.1491	0.6276	0.8745	
S2	$4e$	0.3464	0.1370	0.1769	

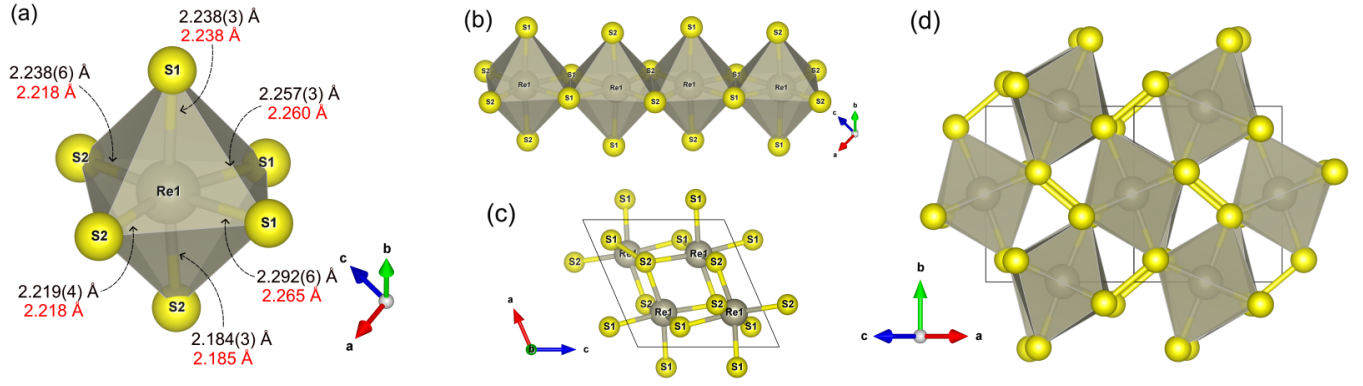


FIG. 2. Crystal structure of the arsenopyrite-type $mP12$ - ReS_2 compound at 54 GPa. Rhenium atoms are shown in grey and sulfur atoms in yellow. (a) A view of the distorted ReS_6 octahedron, where Re-S distances are reported, with experimental values being shown in black and DFT-calculated values in red. (b) A view of the crystal structure showing a row of edge-sharing ReS_6 octahedra running down the [101] direction. (c) A view of the crystal structure along the b axis. (d) A view of the crystal structure along [101], showing the corner-sharing packing of ReS_6 octahedra, as well as the S1-S2 bonds cross linking the rows of ReS_6 octahedra. The black lines in panels (c) and (d) outline the unit cell.

From the atom-projected DOS [Fig. 3(a)], it can be observed that the valence band mainly exhibits a sulfur character, while a Re character dominates between -4 and 0 eV.

Raman spectra collected at 54 GPa are reported in Fig. 4. The violet line in Fig. 4 corresponds to a spectrum collected on the unheated sample, i.e., amorphous CS_2 . The spectrum collected on the laser-heated sample away from the rhenium gasket (orange line in Fig. 4) exhibits the Raman peaks expected for phase II of sulfur [57]. In contrast, where $mP12$ - ReS_2 was observed by XRD, new Raman peaks were measured in addition to those of pure S (see black line in Fig. 4). The additional peaks, centered on the wave-number values 167, 183, 259, 346, 408, 479, 513, and 581 cm^{-1} , are all within 2% of the peak position calculated by DFT (see Fig. 4). These modes can therefore be confidently assigned to the $mP12$ - ReS_2 phase. The calculated frequency and symme-

try of each phononic mode in the $mP12$ - ReS_2 and $aP12$ - ReS_2 phases is tabulated in Tables S1-S4 of the Supplemental Material [53].

B. Decompression and recovery of $mP12$ - ReS_2 to ambient conditions

Figure 5(a) reports the unit cell volume of $mP12$ - ReS_2 as a function of pressure, both from our decompression experiments and DFT calculations. The agreement between the two is excellent. Fitting the experimental pressure-volume data using a second-order Birch-Murnaghan equation of state yields a bulk modulus of $K_0 = 177(9)$ GPa, with V_0/Z being fixed to the experimentally determined value of $46.675 \text{ \AA}^3$, see Fig. S4 of the Supplemental Material [53]. Likewise, $K_0 = 179(1)$ GPa, with V_0/Z being fixed to the DFT-determined

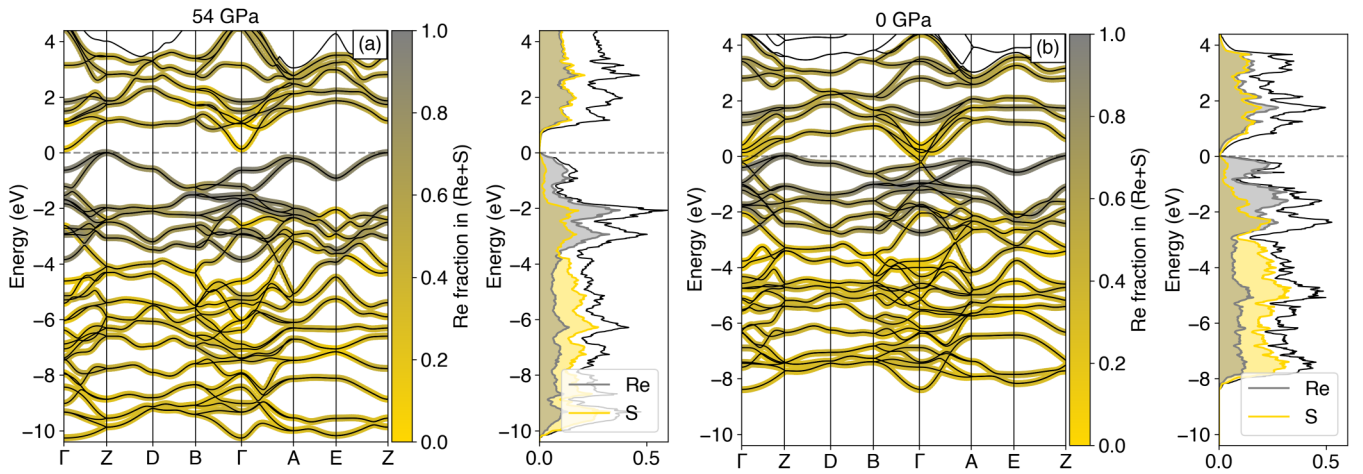


FIG. 3. Electronic band structure and density of states of $mP12$ - ReS_2 at 54 and 0 GPa, calculated using the PBEsol exchange-correlation functional. The horizontal dashed lines indicate the Fermi level. Along the total density of states, the projections onto Re and S atoms are shown as gray and yellow areas, respectively. The electronic band structure is color coded according to the fractional projection $\frac{w_{\text{Re}}}{w_{\text{Re}}+w_{\text{S}}}$, where w_{Re} and w_{S} denote the projections of each Kohn-Sham state onto Re and S atomic orbitals, respectively. Each weight w is obtained by summing over all orbitals and atoms of the corresponding element in the unit cell. The calculations show that the system is a small band gap semiconductor at 54 GPa and a semimetal at 0 GPa.

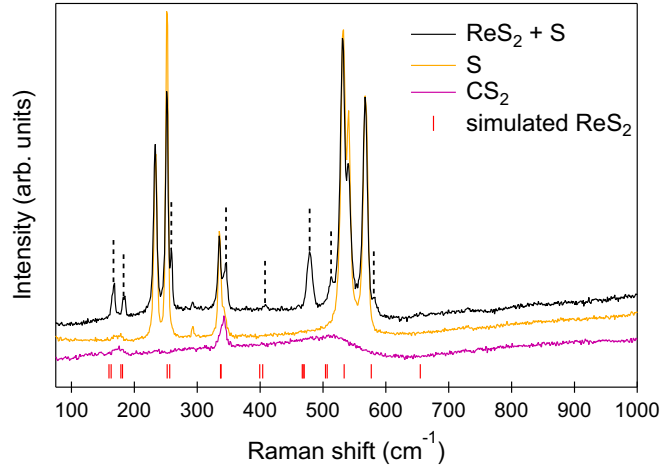


FIG. 4. Experimental Raman spectra of the sample at 54 GPa, corresponding to *mP12*-ReS₂ mixed with pure S (black curve), pure S (orange curve), and unheated CS₂ (violet curve). DFT-calculated Raman frequencies of *mP12*-ReS₂ are shown as red ticks and experimental peaks assigned to *mP12*-ReS₂ are indicated by black dashed vertical lines.

value of 46.483 Å³, is obtained by fitting the DFT-relaxed *mP12*-ReS₂ structures between 0 and 60 GPa. These values are considerably higher than the one obtained for the layered *aP12*-ReS₂ polymorph stable at ambient pressure, i.e., $K_0 = 49(3)$ GPa [35], see also Fig. S4 of the Supplemental Material [53]. This substantial difference in compressibility aligns with the fact that the structure of *mP12*-ReS₂ consists of a three-dimensional framework. High K_0 values can be found in the literature of other three-dimensional transition-metal disulfides; for example, the high-pressure phases of ZrS₂ with space group $P2_1/m$ and $Immm$ have $K_0 = 160(9)$ GPa, $K'_0 = 2.1(4)$ and $K_0 = 172(13)$ GPa, $K'_0 = 1.3(5)$, respectively [58].

Plotting the evolution of the lattice parameters as a function of pressure [Figs. 5(b) and 5(c)] reveals the mildly anisotropic pressure dependence of the crystal structure, with the *b* axis being stiffer than the *a* and *c* axes. The *b* axis is close to being the direction of the long axis of the ReS₆ octahedra and this is presumably the reason why it is stiffer. A similar observation has been reported for the high-pressure arsenopyrite-type phase of MnSe₂ [59]. Regarding the effect of decompression on the interatomic distances, it is found that Re–S contacts are less compressible than S–S ones. Indeed, going from 54 to 0 GPa, Re–S distances elongate by only 5% while S–S distances elongate by 18%, as shown in Fig. 5(d). This anisotropic expansion mechanism observed during sample decompression, driven by the tilting of the ReS₆ octahedra (see Fig. S5 of the Supplemental Material [53]), results in the progressive weakening of the S–S covalent bond until it is absent at ambient pressure. Supporting this assessment is an experimentally determined S–S contact of 2.49(4) Å (2.46 Å from DFT) at ambient pressure—a distance too long to be consistent with S–S bonding [55]. Moreover, calculations (Fig. 6) show a reduction in the electron localization function (ELF) along the S–S contact as pressure decreases, accompanied by the disappearance of the ELF domain in between

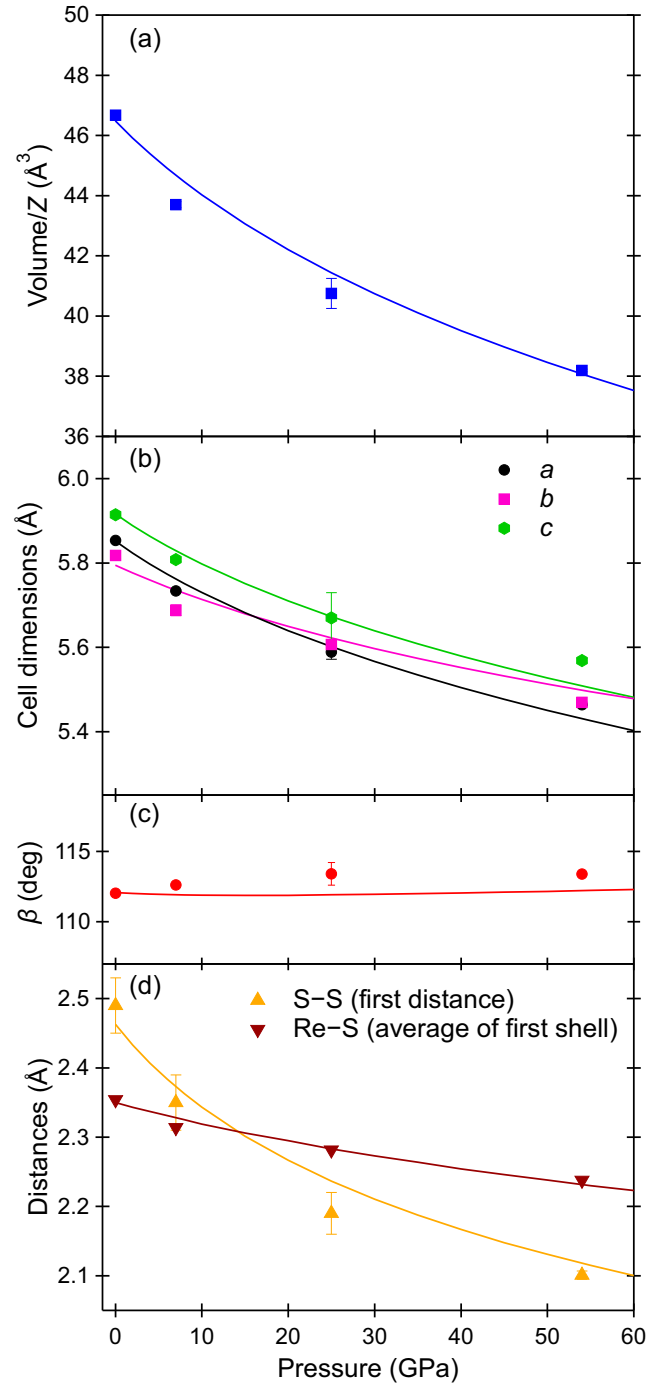


FIG. 5. (a) Pressure dependence of the unit cell volume per formula unit in *mP12*-ReS₂. (b), (c) Pressure dependence of the unit cell parameters in *mP12*-ReS₂. (d) Pressure dependence of the shortest S–S distance and the average Re–S distance within each ReS₆ octahedron in *mP12*-ReS₂. In every panel, experimental results (symbols) are compared to DFT calculations (solid lines).

the S atoms. As a consequence, in the ionic approximation, *mP12*-ReS₂ features [S]^{2−} atoms at ambient pressure. This implies a change in the oxidation state of rhenium, from +2 at 54 GPa to +4 at 0 GPa, yielding Re⁴⁺ ([S]^{2−})₂.

The calculated electronic band structure and density of states of *mP12*-ReS₂ at ambient pressure are shown in

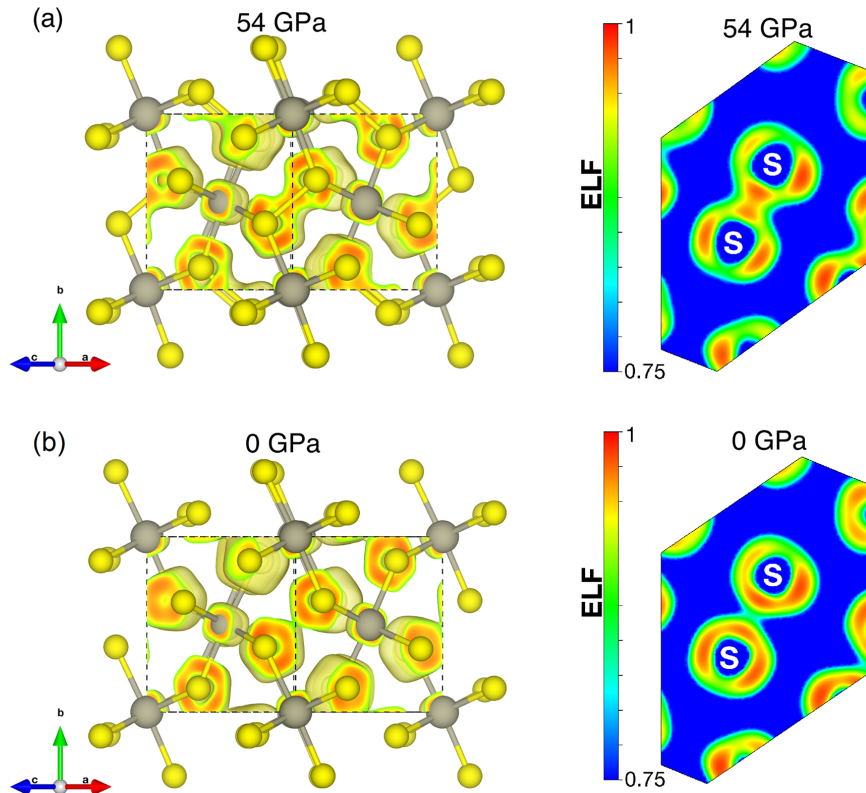


FIG. 6. Calculated electron localization function (left) of *mP12-ReS₂* at 54 and 0 GPa with an isosurface value of 0.8. Rhenium atoms are shown in grey and sulfur atoms in yellow. The origin of the unit cell (black dashed line) has been shifted so that the Re1 atom is at the origin and that the shortest S–S contact is at the center of the unit cell. The projections reported on the right are along a selected plane containing the S–S contact.

Fig. 3(b). The band structure reveals that one band, with predominantly sulfur character, crosses the Fermi level twice around the Γ point. The DOS takes a finite, albeit small, value at the Fermi level, indicating a semimetallic behavior. According to our calculations with the PBEsol exchange-correlation functional, the band gap closes between 30 and 20 GPa upon decompression. In contrast, a direct calculation of the band gap with the Heyd-Scuseria-Ernzerhof functional shifts the gap closing to essentially ambient pressure, where a gap of 85 meV is obtained, well within our resolution (see Fig. S6 of the Supplemental Material [53] for the gap as a function of pressure with both functionals). In any case, both functionals predict an increase in band gap with increasing pressure, which is opposite to the trend observed for most materials. We hypothesize that this behavior is connected with the formation of the S–S bond upon pressure increase. In this picture, the creation of this bond would have consequences on the electronic density of states through the hybridization of the S–S orbitals, leading to the creation of bonding and anti-bonding states that could cause a band-gap opening. Although our evidence does not permit us to draw a definitive conclusion, this behavior represents an unusual feature that merits further investigation. Notably, a similar pressure-induced band-gap opening has been predicted for the arsenopyrite-type phase of TcS_2 [60]. In that case, however, only two pressure points were reported (gap values of 0.513 eV at 0 GPa and 0.785 eV at 20 GPa) and the trend was not discussed.

It is interesting to note the differences and similarities between the known phase of ReS_2 , *aP12-ReS₂*, and the newly identified *mP12-ReS₂*. For that purpose, Figs. 7(a) and 7(b) shows the crystal structure of the layered *aP12-ReS₂* phase, as given in Ref. [28]. Interestingly, *aP12-ReS₂* features the same building blocks as *mP12-ReS₂*, i.e., ReS_6 octahedra also with Re^{4+} cations and S^{2-} anions, where the Re–S bond distances range from 2.312 to 2.504 Å at ambient conditions. These values are comparable with the Re–S bond distances in *mP12-ReS₂* at the same pressure, which are in the range of 2.26(4) to 2.439(16) Å. The shortest S–S contact in the *aP12* phase [i.e., 3.083(7) Å] is also too long to enable bonding between these atoms. The arrangement of the ReS_6 units in *aP12-ReS₂* differs from that of *mP12-ReS₂*, as they share six edges with adjacent octahedra and form sheets lying in the *b-c* plane [Fig. 7(b)]. Notably, the experimental density of *mP12-ReS₂* (8.90 g/cm³) at ambient conditions is 17.4% larger than that of the *aP12-ReS₂* polymorph (7.58 g/cm³) [28]. Comparing DFT-calculated densities, the difference is even slightly larger, i.e., 20.8% (8.94 g/cm³ for the *mP12* phase and 7.40 g/cm³ for the *aP12* phase).

Also in Fig. 7, the DFT-calculated enthalpy difference between the two ReS_2 polymorphs is provided. The *aP12-ReS₂* phase is found to be more stable at ambient pressure (as expected) but, interestingly, the *mP12-ReS₂* polymorph is a mere 4 meV/atom higher in energy [Fig. 7(c)]. Moreover, the latter becomes thermodynamically favored over the former at pressures above 0.3 GPa [Fig. 7(c)]. Given such a

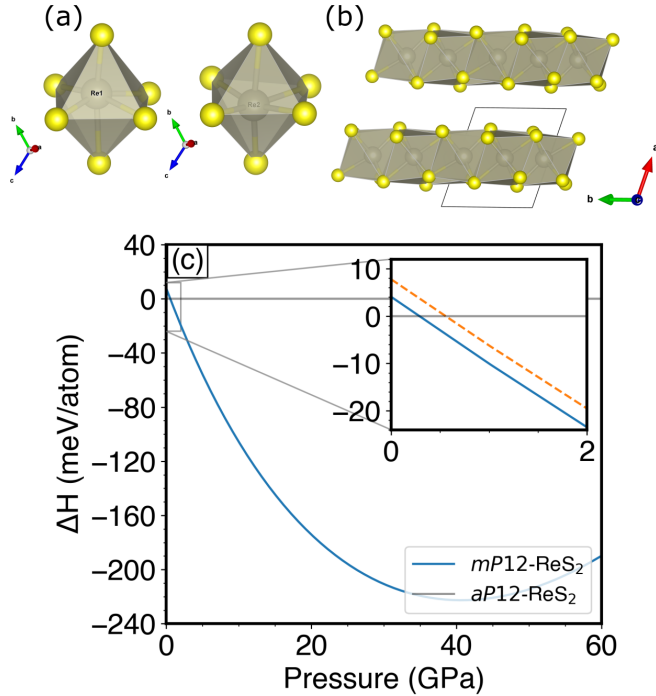


FIG. 7. (a), (b) Crystal structure of $aP12\text{-ReS}_2$ (space group $P\bar{1}$) at ambient pressure from Ref. [28], which exhibits a laminar structure. Rhenium atoms are shown in grey and sulfur atoms in yellow. (a) A view of the two inequivalent distorted ReS_6 octahedra. (b) A view of the crystal structure along the c axis, showing two identical layers. (c) Calculated enthalpy ΔH of the $mP12\text{-ReS}_2$ polymorph relative to the $aP12\text{-ReS}_2$ polymorph. Negative values of ΔH indicate that $mP12\text{-ReS}_2$ is more stable than $aP12\text{-ReS}_2$. The inset shows a zoomed-in region for pressures below 2 GPa, where the dashed orange line corresponds to the result corrected for the estimated zero-point energy.

small energy separation, the $mP12\text{-ReS}_2$ phase is likely to be metastably accessible at ambient conditions [5]. Its formation is certainly achievable using industrial-scale devices such as piston-cylinder or belt-type large-volume high-pressure presses, and possibly even at ambient pressure in the presence of suitable catalysts. Finally, it should be noted that energies of the order of meV/atom are essentially within the typical uncertainties of the calculations. In fact, the energy difference at 0 GPa increases from 4 to 7.7 meV/atom when the zero-point energy of both phases is also taken into account. Similarly, the crossover pressure increases from 0.3 GPa to 0.6 GPa (see the inset of Fig. 7(c) and Table S5 of the Supplemental Material [53]).

C. Comparison with previous high-pressure studies

Remarkably, no arsenopyrite-type phase of ReS_2 had been considered as a candidate or found by structure-search calculations in previous high-pressure computational studies [36,37]. One may also wonder why the previous high-pressure experiments [30–35] on ReS_2 did not find the arsenopyrite-type phase reported in the present work. The core difference is that the samples in those experiments were not subjected to laser heating, thus preventing the crossing

of the activation barrier between the two phases. Indeed, the significant rearrangement of the ReS_6 units necessary to convert a layered structure into a three-dimensional arrangement likely results in a large kinetic-energy barrier [61]. The high-pressure literature is replete with examples where high temperature has been shown to be essential for crossing energy barriers and reaching the phase thermodynamically most stable [62,63].

In fact, such examples even extend to TMDs. Indeed, arsenopyrite-type phases of MnS_2 and TcS_2 were produced upon laser heating at 20 and 30 GPa, respectively [60,64]. Upon decompression, the arsenopyrite-type polymorph of MnS_2 underwent a reverse transformation to the ambient-pressure (pyrite-type) structure between 5 and 1 GPa [64]; however, the arsenopyrite-type polymorph of TcS_2 was recovered down to ambient conditions, based on Raman data [60]. The formation of these compounds also highlights a clear systematic crystal-chemical trend for group 7 transition-metal disulfide compounds, with Re, Tc, and Mn all being part of that same column of the Periodic Table. Still, interesting differences remain between these solids since MnS_2 , TcS_2 , and ReS_2 do not adopt the same structure at ambient conditions, with MnS_2 not even producing a layered structure.

We are not aware of any literature reports on the synthesis of any other Re dichalcogenide polymorph having the arsenopyrite structure type, whether at ambient or high pressure. Such a possibility remains to be explored in the future, particularly for ReSe_2 , which is isostructural to ReS_2 at ambient conditions, and particularly so as the high-pressure arsenopyrite-type polymorph of MnSe_2 is known to exist [59].

IV. CONCLUSIONS

In summary, a ReS_2 polymorph ($mP12\text{-ReS}_2$) with the three-dimensional arsenopyrite structure type (space group $P2_1/c$) was observed to form upon laser heating of CS_2 and Re at 54 GPa in a diamond anvil cell. Raman peaks of this new phase were identified experimentally at 54 GPa and show excellent agreement with the DFT-calculated Raman-active modes. At 54 GPa, $mP12\text{-ReS}_2$ is comprised of persulfide anions (S–S distance of ~ 2.1 Å), indicative of a Re^{2+} oxidation state. Notably, this compound does not correspond to any of the ReS_2 phases previously predicted to be stable at high pressures [36,37]. Polymorphs of MnS_2 and TcS_2 with the same arsenopyrite structure type have been reported to form under high-pressure and high-temperature conditions [60,64], revealing a consistent trend for group 7 elements with sulfur.

Upon decompression, the equation of state of the novel $mP12\text{-ReS}_2$ polymorph was determined, and the phase was found to be recoverable down to ambient conditions and stable in air. Both experimental data and DFT calculations demonstrate that the high-pressure $mP12\text{-ReS}_2$ polymorph is significantly denser and less compressible than the ambient-pressure $aP12\text{-ReS}_2$ phase [28], with a bulk modulus nearly four times larger. During decompression, anisotropic lattice expansion driven by the tilting of ReS_6 octahedra results in the progressive weakening and eventual disappearance of the S–S bonds, accompanied by a change in rhenium's oxidation state from +2 to +4 in the ionic approximation. Electronic-structure calculations indicate that the new phase is a small

band gap semiconductor at 54 GPa and becomes semimetallic at ambient pressure (or near-semimetallic, depending on the employed functional).

Finally, $mP12\text{-ReS}_2$ is calculated to be metastable with respect to the literature phase $aP12\text{-ReS}_2$ [28] at ambient pressure, becoming energetically favored above a moderate pressure of ~ 0.5 GPa. As the $mP12\text{-ReS}_2$ phase has not been reported before in the experimental high-pressure literature [30–35], its formation is likely kinetically hindered, requiring high temperature to overcome the associated energy barrier. These results provide new insight to understand the structural behavior and physical properties of TMDs under extreme conditions and, given the presumed synthesizability of $mP12\text{-ReS}_2$ employing a large-volume press, provide a strong drive to further investigate its properties at ambient conditions.

ACKNOWLEDGMENTS

We acknowledge the European Synchrotron Radiation Facility (ESRF) for provision of synchrotron radiation facilities, and we thank James Ball for assistance in using the ID11 beamline and Gaston Garbarino for assistance in using the laser-heating setup. We also acknowledge the Deutsches Elektronen-Synchrotron (DESY) for granting syn-

chrotron beamtime at the P02.2 beamline and Bihan Wang for assistance. We thank Katalin Kis (CSEC) for help with safety aspects related to loading the sample. Funding for this research was provided by the UK Research and Innovation, Future Leaders Fellowship (Grant No. MR/V025724/1 to D. Laniel). S.D.C. acknowledges computational resources from the EuroHPC project “EXCHESS” (Grant No. EHPC-REG-2024R01-089) and funding from the European Union - NextGenerationEU under the Italian Ministry of University and Research (MUR), “Network 4 Energy Sustainable Transition - NEST” project (MIUR Project No. PE000021, Concession Degree No. 1561 of October 11, 2022) - CUP B53C2200407000.

DATA AVAILABILITY

The experimental crystal structures at 54 GPa and ambient pressure are openly available from the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures Service, under the deposition numbers 2502668 and 2502672, embargo periods may apply. Other data are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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