Electronic Supplementary Material (ESI) for Materials Advances.

$Tl_{0.6}Mo_3S_5$, an original large tunnel-like molybdenum sulfide with Mo zigzag chains and disordered Tl cations

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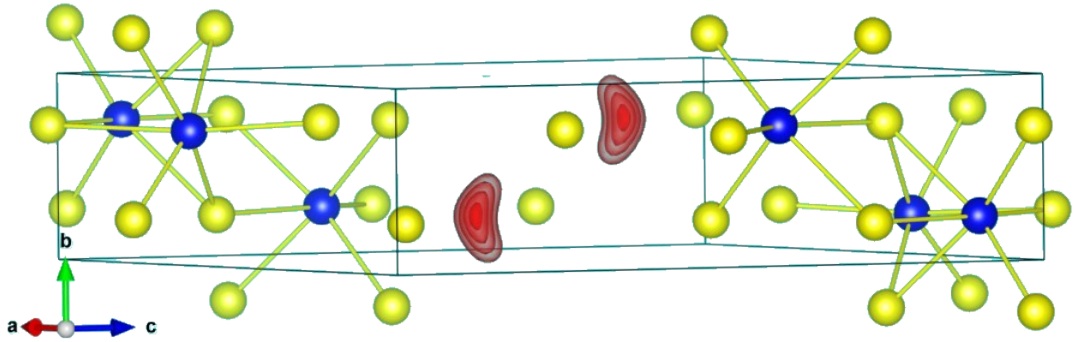

Figure S1. 3D isosurface of the Fourier difference maps showing the bean-shaped electronic density of Tl after refinement of the Mo-S framework (isosurface levels at 20, 30, 40 and 50 e/Å^3 from light to dark red, Mo and S atoms are shown in blue and yellow, respectively).

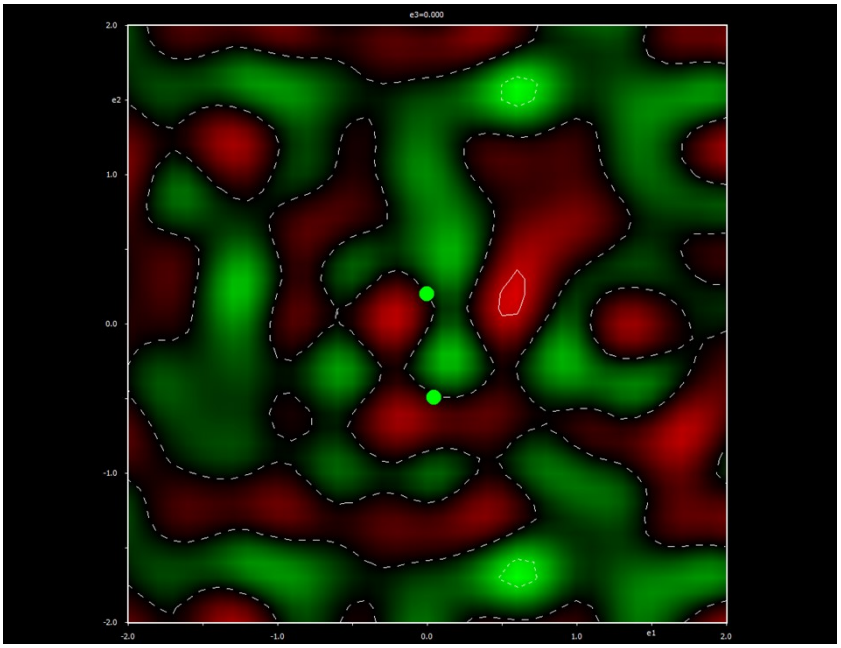

Figure S2. Fourier difference maps along the *b* axis in $Tl_{0.6}Mo_3S_5$ near the Tl cations after the final refinement (step: 1 eÅ^{-3}).

Table S1. Relevant Parameters of the Single Crystal Data Collection and Structure Refinement of the Average Crystal Structure of $Tl_{0.58}Mo_3S_5$.

Empirical formula	$Tl_{0.58}Mo_3S_5$
Molar mass (g.mol^{-1})	566.65
Temperature	293(2) K
Symmetry	Monoclinic
Space group	$P2_1$
a, b, c (Å)	9.344(2), 3.234(2), 11.669(2)
β (°)	113.09(2)
V (Å^3)	324.4(2)
Z	2
ρ (calculated, g.cm^{-3})	5.802
F(000)	506
Crystal size (mm^3)	0.08 × 0.07 × 0.06
Radiation	Mo $K\alpha$ (0.71069 Å)
θ range (°)	1.897 – 34.962
Absorption coefficient (mm^{-1})	21.53
Limiting indices	-15≤ h ≤15, 0≤ k ≤5, −18≤ l ≤18
Reflection collected	3262
Independent reflections	1632 [R(int) = 0.0377]
Completeness to θ = 25.241°	100%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1632 / 1 / 94
Final R indices [I>2σ(I)]	R1=0.0334, wR2=0.0611
R indices (all data)	R1=0.0604, wR2=0.0686
Absolute structure parameter	0.10(4)
Extinction coefficient	0.0020(5)
Largest diff. peak and hole	1.607 and −1.984 eÅ^{-3}
Goodness-of-fit on F^2	1.049

Table S2. Fractional Atomic Coordinates and Isotropic Thermal Displacement Parameters (in Å^2) for the Average Crystal Structure of $Tl_{0.58}Mo_3S_5$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq} (Å^2)	*s.o.f.*
Mo1	0.9848(1)	0.2435(13)	0.3992(1)	0.011(1)	1
Mo2	0.3691(1)	0.2348(14)	0.9893(1)	0.014(1)	1
Mo3	1.0015(1)	0.2483(12)	0.9010(1)	0.010(1)	1
S1	0.8644(2)	0.2480(20)	0.6677(1)	0.009(1)	1
S2	0.4987(2)	0.2570(30)	0.8546(2)	0.011(1)	1
S3	0.1903(2)	0.2360(20)	0.1109(1)	0.008(1)	1
S4	0.1997(2)	0.2460(30)	0.5913(1)	0.010(1)	1
S5	0.8273(2)	0.2480(20)	0.1556(1)	0.007(1)	1
Tl1	0.5385(7)	−0.1690(30)	0.6321(5)	0.056(3)	0.235(14)
Tl2	0.5386(7)	−0.3740(50)	0.6179(8)	0.102(4)	0.342(14)

Table S3. Anisotropic Thermal Displacement Parameters for the Average Crystal Structure of $Tl_{0.58}Mo_3S_5$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo1	0.0064(2)	0.0210(3)	0.0051(2)	0.0015(9)	0.00170(16)	-0.0009(11)
Mo2	0.0051(2)	0.0316(5)	0.0056(2)	0.0004(9)	0.00182(17)	0.0015(10)
Mo3	0.0051(2)	0.0195(4)	0.0054(2)	-0.0027(8)	0.00245(16)	-0.0060(9)
S1	0.0118(6)	0.0096(8)	0.0064(6)	0.0053(19)	0.0035(5)	0.007(2)
S2	0.0200(7)	0.0057(10)	0.0132(6)	-0.0017(18)	0.0117(6)	0.003(2)
S3	0.0073(6)	0.0067(9)	0.0087(6)	0.0043(19)	0.0013(5)	-0.001(2)
S4	0.0104(6)	0.0075(8)	0.0088(6)	-0.003(2)	-0.0003(5)	0.000(3)
S5	0.0088(6)	0.0077(7)	0.0065(5)	-0.005(2)	0.0038(5)	-0.001(3)
Tl1	0.038(2)	0.106(6)	0.0136(14)	-0.0260(18)	-0.0004(10)	0.022(2)
Tl2	0.071(3)	0.164(9)	0.055(3)	0.048(4)	0.0082(18)	0.006(3)

Table S4. Selected Interatomic Distances (in Å) for the Average Crystal Structure of $Tl_{0.58}Mo_3S_5$.

Mo1-S4		Tl1-S2	
Mo1-S4		Tl1-S3	
Mo1-S4		Tl1–S1	
Mo1-S1		Tl1–S4	
Mo1-S1		Tl1-S2	
Mo1-S5		Tl1-S1	
Mo1-Mo1		Tl1-S4	
Mo1-Mo1		Tl1-S1	
Mo2-S2		Tl2-S1	
Mo2-S2		Tl2-S2	
Mo2-S2		Tl2-S3	
Mo2-S5		Tl2-S4	
Mo2-S5		Tl2-S1	
Mo2-S3		Tl2-S2	
Mo2-Mo2		Tl2-S4	
Mo2-Mo2		Tl2-S1	
Mo2-Mo3			
Mo3-S3			
Mo3-S3			
Mo3-S3			
Mo3-S1			
Mo3-S5			
Mo3-S5			
Mo3-Mo3			
Mo3-Mo3			

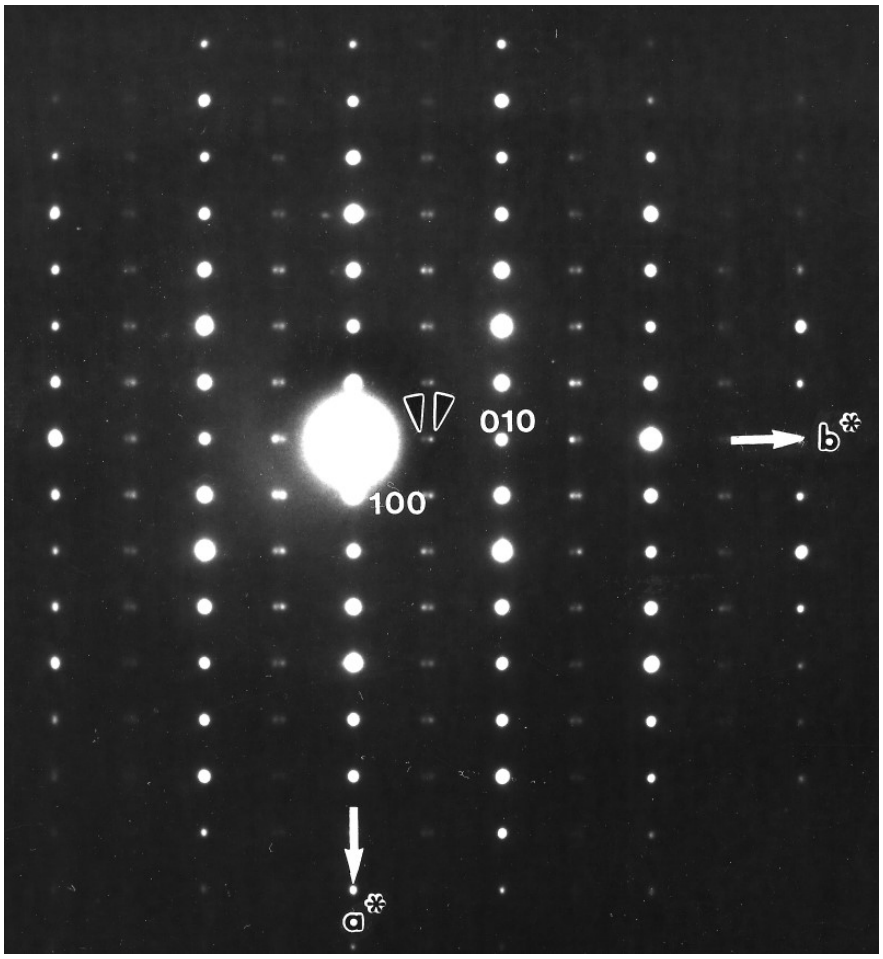

Figure S3. Electron diffraction images collected on crushed polycrystalline $Tl_{0.6}Mo_3S_5$ in the *ab* plane. In addition to the main reflections, two rows of additional reflections (marked the black arrowheads) are observed, suggesting the presence of an incommensurate modulation running along the *b* axis.

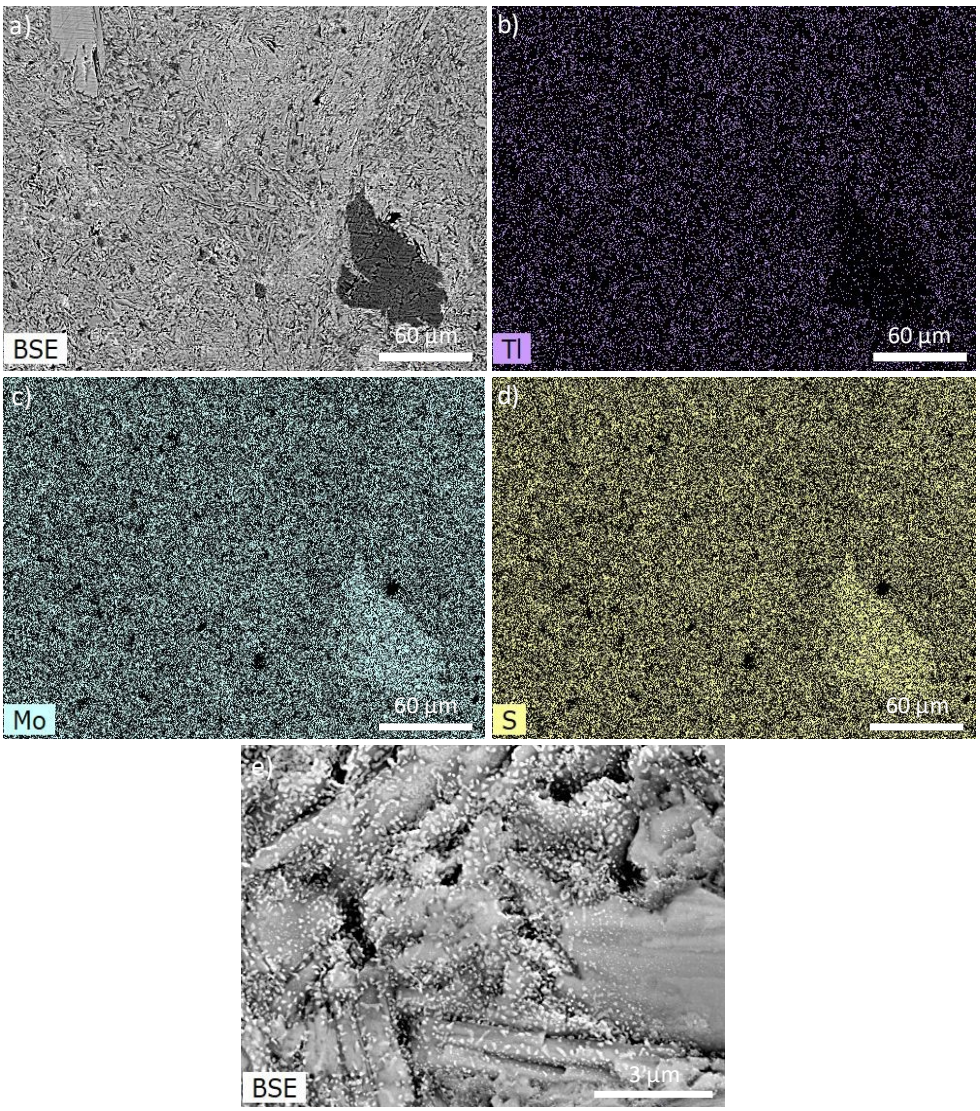

Figure S4. a) Backscattered electron image (BSE) collected on a dense, bulk polycrystalline piece of $Tl_{0.6}Mo_3S_5$, showing the presence of a minute amount of MoS_2 used as a precursor to synthesize this compound. Their small concentration is not expected to significantly alter the measured transport properties. The corresponding elemental X-ray maps are shown in panels b), c), and d). e) BSE image taken at higher magnification showing the presence of grains decorated by nanoparticles.

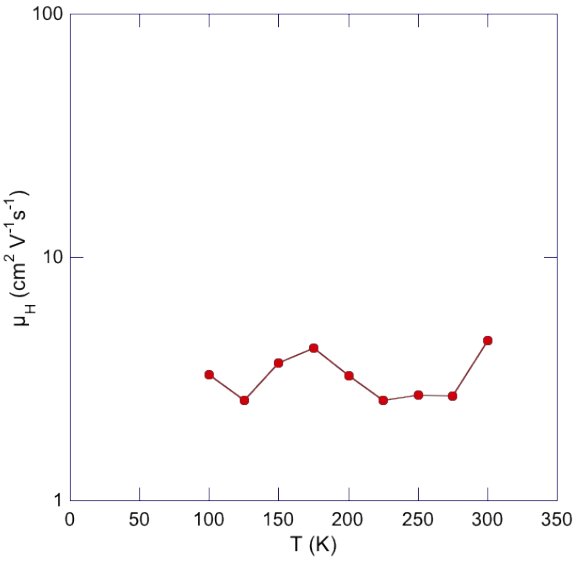

Figure S5. Temperature dependence of the Hall mobility μ_H.