Critical enhancement of thermopower in a chemically tuned polar semimetal MoTe₂

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Ferroelectrics with spontaneous electric polarization play an essential role in today's device engineering, such as capacitors and memories. Their physical properties are further enriched by suppressing the long-range polar order, as exemplified by quantum paraelectrics with giant piezoelectric and dielectric responses at low temperatures. Likewise in metals, a polar lattice distortion has been theoretically predicted to give rise to various unusual physical properties. However, to date, a “ferroelectric”-like transition in metals has seldom been controlled, and hence, its possible impacts on transport phenomena remain unexplored. We report the discovery of anomalous enhancement of thermopower near the critical region between the polar and nonpolar metallic phases in 1T'-Mo₁₋ₓNbₓTe₂ with a chemically tunable polar transition. It is unveiled from the first-principles calculations and magnetotransport measurements that charge transport with a strongly energy-dependent scattering rate critically evolves toward the boundary to the nonpolar transition. Such a significant influence of the structural instability on transport phenomena might arise from the fluctuating or heterogeneous polar metallic states, which would pave a novel route to improving thermoelectric efficiency.

INTRODUCTION

A “ferroelectric”-like transition in metals was first predicted by a pioneering work (1) in the 1960s, followed by the predictions of fascinating physical properties of a polar metal, such as unconventional superconductivity (2), magneto-optical effects (3), and highly anisotropic thermopower (4). However, at present, there are few reported metallic materials exhibiting a polar structural transition (5–9). In particular, control of the structural transition temperature has remained an experimental challenge which would enable the search for novel quantum phenomena associated with the criticality of the polar, that is, “ferroelectric”-like, transition in metals.

To seek an ideal metallic system with a chemically tunable polar structural transition, we focused on transition metal dichalcogenides (TMDs). TMDs have attracted renewed interest because of a rich variety of electronic properties, which are associated with large structural variations ranging from chemically controllable bulk forms to mechanically exfoliated single- or a few-layers (10, 11). Among metallic TMDs, 1T'-MoTe₂ [for example, M = Mo (12–15) and W (16)] has gained great attention, spurred by the discoveries of extremely large magnetoresistance effects (17, 18) and pressure-induced superconductivity (19–21) and by the prediction of Weyl semimetallic (22, 23) and quantum Hall insulating states (24). 1T'-MoTe₂ crystallizes in a CdI₂-type structure consisting of edge-sharing MoTe₆ octahedra with a strong distortion, which is caused by the formation of zigzag chains of metal-metal bonding along the b axis (as enclosed by dashed ellipses in Fig. 1A) (25). However, at room temperature, the crystal structures for 1T'-MoTe₂ and 1T'-WTe₂ differ from each other (25, 26); the former is monoclinic (P2₁/m; Fig. 1A, right) and the latter is orthorhombic (Pnma) (Fig. 1A, left). Note that 1T'-WTe₂ has a polar (noncentrosymmetric) space group, which results in the Weyl semimetallic state (27). For 1T'-MoTe₂, on the other hand, it was reported that the centrosymmetric monoclinic structure at room temperature changes to an orthorhombic structure at 250 K (28, 29), which may be identical to that for 1T'-WTe₂. Therefore, 1T'-MoTe₂ is a promising candidate of the metallic system, allowing chemical control of a polar structural transition.

RESULTS

Chemically tunable polar transition in a metal

To demonstrate the tuning of the putative polar structural transition at ~250 K in 1T'-MoTe₂, we prepared single-crystalline samples of Mo₁₋ₓNbₓTe₂ (for chemical composition determination, see fig. S1 and Materials and Methods) and performed the x-ray diffraction measurements at selected temperatures. The panels in the inset to Fig. 1B present the charge-coupled device (CCD) images of Bragg reflections [0 1 3] and [1 0 13] that are sensitive to the symmetry change, where the horizontal direction corresponds to the Bragg angle. Upon cooling for x = 0, the two reflections that were clearly split up by the monoclinic distortion at 300 K approach each other at 250 K and coalesce to become a single 1 0 13 reflection below 200 K, indicating a transition to an orthorhombic phase (28, 29).

A single-crystal x-ray structural analysis at 100 K has revealed that the space group of the low-temperature phase is orthorhombic Pnma, where the polar direction is along the c axis (Fig. 1A and see table S1 for details). Here, we will emphasize that the polar transition temperature in metallic 1T'-MoTe₂ can be systematically tuned from ~250 K down to 0 K by chemical substitution of Nb for Mo. As shown in the inset to Fig. 1B, for x = 0.08, the temperature below which two split Bragg reflections coalesce is lowered by more than 50 K compared to the pristine x = 0 compound. For x = 0.22, the structural transition is further suppressed; the Bragg spots remain to be split even at 100 K. The suppression of the polar transition can be associated with a monotonic decrease in interlayer distance at x = 0.22 because the interlayer distance unusually increases with decreasing temperature across the polar transition (28). This is apparently consistent with the fact that the external pressure reduces the polar transition temperature for 1T'-MoTe₂ (19–21).
Fig. 1. Tunable polar structural transitions. (A) Lattice structures for 1T-MoTe₂ at 100 K (left) and 300 K (right), deduced from structural analyses based on single-crystal x-ray diffraction. Mo-Mo bonds enclosed by dashed ellipses form a zigzag chain of Mo atoms along the b axis (see also fig. S8). The Te ions are color-coded depending on the crystallographic sites. Small black arrows near the Te ions schematically denote the displacements relative to the center of Mo ions in the low-temperature orthorhombic phase. (B) The contour plot of S/T (thermopower divided by temperature) and structural phase diagram as functions of temperature T and Nb concentration x for 1T-Mo₁₋ₓNbₓTe₂. The circles and squares denote the transition temperatures Tₛ determined by the resistivity and optical second-harmonic generation (SHG), respectively. The open and closed symbols correspond to the cooling and warming runs, respectively. The gray line is a guide to the eyes. Inset displays the temperature variation of single-crystal x-ray diffraction images around the 1 0 1₃ and 1 0 1₄ reflections in the monoclinic phase for x = 0, 0.08, and 0.22. These Bragg reflections coalesce into 1 0 1₃ in the orthorhombic phase. The direction of the horizontal arrow on the photograph corresponds to that of 20° of the diffractometer.

The resultant structural phase diagram is shown in Fig. 1B, where the transition temperature Tₛ is precisely determined by the transport and optical measurements (vide infra). The value of Tₛ gradually decreases with increasing x, followed by an immediate drop to 0 at around x = 0.1. For x = 0.12, the polar orthorhombic phase is replaced by the nonpolar monoclinic phase at the ground state, forming a critical state between the polar and nonpolar metals. Note here that such a controllable polar transition is quite rare in metallic systems, considering that even in degenerately doped ferroelectrics, such as oxygen-deficient and La-doped BaTiO₃ (8, 9), the ferroelectric transition temperature remains nearly constant (above 250 to 300 K) upon carrier doping. Below, we shall present a marked impact of tuning the polar transition on the transport and optical properties.

Figure 2A shows the temperature profile of resistivity for 1T-Mo₁₋ₓNbₓTe₂ with x ranging from 0 to 0.22. The x = 0 compound exhibits good metal behavior with the residual resistivity ρ₀ = 5.9 µΩ cm at 2 K, resulting in a ratio of the resistance at room temperature to that at 2 K of ~65. A clear resistivity anomaly at a Tₛ (~250 K) with a thermal hysteresis (denoted by arrows) reflects the first-order nature of the polar structural transition. As x increases to 0.08, the values of Tₛ defined by the resistivity anomalies decrease, accompanied by large thermal hysteresis between the cooling and heating runs. For x ≥ 0.12, no anomaly is observed down to the lowest temperature, indicating that the polar structural transition is completely suppressed. The variation of ρ₀ is nonmonotonic as a function of x; it rapidly increases from 5.9 to 177 µΩ cm with increasing x from 0 to 0.08, followed by a decrease by about half for x = 0.12. For x ≥ 0.12, ρ₀ is almost independent of x. The anomalous x dependence of ρ₀ cannot be simply explained by the impurity scattering due to the doped Nb ions but may be relevant to the critical enhancement of charge scattering around x = 0.08, as discussed below.

Figure 2B presents the temperature profile of optical SHG intensity for the samples with selected compositions. Strong SHG signals are observed for x = 0 and 0.08 below Tₛ but not for x = 0.22, which supports the absence and presence of inversion symmetry in the orthorhombic and monoclinic phase, respectively. The detailed SH polarization patterns are consistent with the point group symmetry mm2 inferred from the crystal structural analysis (fig. S2, C and D) and the recent Raman spectroscopy (30, 31). The estimated nonlinear optical susceptibility is comparable in magnitude to the d₁₁ of quartz (see the Supplementary Materials). Note here that the temperature dependence of the SHG intensity for x = 0.08 markedly differs from that for x = 0. For x = 0.08 with a lower Tₛ, the transition accompanied by a significant thermal hysteresis appears to be more diffusive; the nonzero SHG intensity remains even
above $T_S$. Furthermore, the SHG intensity decreases with decreasing temperature below ~150 K, which signals that the polar phase tends to be reduced in volume fraction, or fluctuated at low temperatures, because the Nb concentration is close to the critical value at the phase boundary ($x \sim 0.1$).

On the basis of the rigid-band scheme, the Nb substitution for Mo should decrease the Fermi energy, leading to the hole carrier doping. This tendency is confirmed in the $x$ variation of Hall resistivity $\rho_{yx}$ as shown in Fig. 3B. For $x = 0$, the field profile of $\rho_{yx}$ is curved with a negative slope and is strongly temperature-dependent, which is typical of a semimetal with multicarriers with opposite polarity. This is consistent with the results of first-principles calculations, which predict the formation of small electron and hole pockets (Fig. 4D, $x = 0$), as is the case for $\text{WTe}_2$ (17). Note here that a large magnetoresistance effect was also observed (~300% at 2 K at 9 T) for $x = 0$ (Fig. 3B, inset). For $x = 0.08$ and 0.22, on the other hand, the field profile of $\rho_{yx}$ becomes straight, with a positive slope for all temperatures, and the magnetoresistance effect is largely suppressed. This indicates that only hole-like carriers exist for $x \geq 0.08$, as schematically described in Fig. 4D ($x = 0.1$ and 0.2). The Hall coefficient is almost temperature-independent for $x = 0.22$, as is common for simple metals. However, for $x = 0.08$, it exhibits an unusual temperature dependence; the value almost triples as the temperature decreases from 300 to 2 K.

**Thermopower enhancement near the critical region**

The most marked impact of the suppression of the polar transition in $1T’$-$\text{MoTe}_2$ is found in thermopower $S$ at low temperatures (Fig. 3A). For $x = 0$, the value of $S$ remains small over the entire temperature range, reflecting the semimetallic band structure, where the electron- and hole-like carriers compensate each other. The polar transition is discernible as a clear drop in $S$ upon cooling with a thermal hysteresis, as denoted by arrows. With increasing $x$, the positive value of $S$ progressively increases because the hole-like carriers become dominant. What is prominent is the temperature profile of $S$ for $x = 0.08$; the $S$ value unusually increases up to as much as 85 $\mu$V/K with decreasing temperature down to ~50 K, followed by a steep decrease down to 0 toward the lowest temperature. The evolution of $S$ toward low temperatures tends to be weakened as $x$ increases from 0.08 to 0.15. Consequently, the $x = 0.15$ sample shows a peculiar temperature profile of $S$ that is almost constant (~65 $\mu$V/K) between 60 and 300 K. By further increasing $x$ up to 0.22, the value of $S$ decreases across all temperature ranges, and the temperature dependence becomes monotonic.

A more suggestive presentation of the thermopower data is the contour plot of $S/T$ as functions of $x$ and $T$, shown in Fig. 1B, because the quantity of $S/T$, relevant to both transport and thermodynamic properties, should be temperature-independent for the conventional Fermi liquid systems (see Eq. 1). Near the phase boundary between polar orthorhombic and nonpolar monoclinic phases, the $S/T$ magnitude evolves toward the lowest temperature to form a red dome-shaped distribution around $x = 0.1$. In this "hot" region, we observed distinct behavior in other physical properties as well, such as a large increase in $\rho_0$ and $\rho_{yx}$ and a reduction in SHG intensity, as mentioned above. Below, we discuss their possible origin in terms of anomalous scattering promoted near the critical regime between the polar and nonpolar phases.

**Comparison with theoretical calculations**

Figure 4 (A and B) presents the full landscape of $S$ for $1T’$-$\text{Mo}_{1-x}\text{Nb}_x\text{Te}_2$ obtained through experiments and calculations, respectively. At high temperatures, the first-principles calculations roughly reproduce the $x$ dependence of the experimental $S$ value, which are featured by the broad hump-like structure around $x = 0.1$ to 0.15. At low temperatures, on the other hand, the calculated results largely deviate from the experimental ones. The characteristic $S$ hump observed at low temperatures near $x = 0.1$ is not reproduced by the calculations; the calculated $S$ value is only $1/10$ of that measured below 50 K. Note here that the electronic specific heat coefficient $\gamma$ is nearly constant ($\gamma \sim 3$ mJ/mol K$^2$ in experiments) as a function of $x$ (Fig. 4B, inset, and Fig. S3), indicating that the $S$ enhancement observed below 50 K does not originate from an anomaly in band structure, that is, electronic density of states. Furthermore, the almost $x$-independent profile of $\gamma$ is theoretically reproduced (Fig. 4B, inset), which affirms the validity of the first-principles calculation for the band structure in the present systems. (The experimental $\gamma$ values that are larger than the theoretical values may arise from the renormalization due to the electron-phonon and/or electron-electron interactions.)

To seek the origin of the discrepancy in the $S$ profiles, we now consider the diffusion thermopower based on the Mott formula

$$S = -\frac{\pi^2 k_B^2 T}{3} \frac{\partial \ln \sigma(\epsilon)}{\partial \epsilon} |_{\epsilon = \epsilon_F}$$

where $\sigma$ is the dc electrical conductivity tensor, $k_B$ is the Boltzmann constant, and $\epsilon_F$ is the Fermi energy. Assuming a simple relation $\sigma \sim v \tau S_0$, with $v$, 

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**Fig. 3. Variation of thermopower and Hall resistivity.** (A) Temperature profile of thermopower $S$ along the $b$ axis for $1T’$-$\text{Mo}_{1-x}\text{Nb}_x\text{Te}_2$ single crystals. (B) Magnetic field profile of Hall resistivity $\rho_{yx}$ at various temperatures for $x = 0$ (left), 0.08 (middle), and 0.22 (right). Inset shows the magnetoresistance effect $\Delta \rho_{yx}(B)/\rho_{yx}(0) = |\rho_{yx}(B) - \rho_{yx}(0)|/\rho_{yx}(B = 0)$ as a function of field at 2 K for $x$ from 0 to 0.22.
Fig. 4. Comparison between the experimental and theoretical results on thermopower and electronic structures. (A and B) Experimental (A) and theoretical (B) thermopower $S$ as functions of temperature $T$ and Nb concentration $x$ for 1T'-Mo$_{1-x}$Nb$_x$Te$_2$. The calculations were performed based on the orthorhombic polar structure. (Quantitatively similar calculation results were obtained for the monoclinic structure, as shown in fig. S9.) Inset displays the $x$ dependence of electronic specific heat coefficient $\gamma$, deduced from experiments (closed circles) and from first-principles calculation (open circles). (C) Experimental thermopower for polycrystalline W$_{1-x}$Ta$_x$Te$_2$ is plotted as functions of temperature and Ta concentration $y$. (D) The calculated Fermi surface of 1T'-Mo$_{1-x}$Nb$_x$Te$_2$ with the orthorhombic structure for $x = 0.0, 0.1,$ and $0.2$, showing electron (blue) and hole (red, green, and magenta) pockets. Because the orthorhombic phase has no inversion symmetry, the Fermi surface sheets are doubled (each corresponding to one spin state). For the difference in band structure between the polar (orthorhombic) and nonpolar (monoclinic) structures, see fig. S10.

$\tau$, and $S_F$ being the Fermi velocity, (energy-dependent) relaxation time, and Fermi surface area, respectively, we obtain

$$S = -\frac{\pi^2 k_B^2 T}{3e} \left( \frac{\partial \ln (\gamma S_F)}{\partial \epsilon} + \frac{\partial \ln \tau}{\partial \epsilon} \right)_{\epsilon = \epsilon_F} \tag{2}$$

In the present calculation, the first component associated with the band structure is fully taken into consideration, whereas the second one, which stems from the charge relaxation due to scattering, is ignored by adopting the constant $\tau$ approximation. The deviation of the experimental results from the calculated ones is hence attributable to the dominant contribution from the latter scattering term with strongly energy-dependent $\tau(\epsilon)$.

A similar peak structure in the $S$ profile is often observed at low temperatures as a manifestation of a phonon drag effect, which is, however, not the case here. This is because the polycrystalline samples of doped MoTe$_2$ exhibit essentially the same $S$ profiles as functions of $x$ and $T$, irrespective of substitution species, Nb or Ta (fig. S4). In general, the phonon drag effect tends to be appreciable at low temperatures in clean systems, where phonons are mostly scattered by electrons via the electron-phonon interaction. In the polycrystalline samples, because phonons are primarily scattered by grain boundaries and doped impurities, the phonon drag thermopower would be negligibly small and hence could not explain the observed $S$ enhancement insensitive to the phonon scattering.

**DISCUSSION**

It was recently reported that thermoelectric contribution from the second term in Eq. 2 can be dominant in some systems, including heavy fermion compounds (32, 33) and correlated semiconductors (34). In these materials, the highly dispersive $\tau(\epsilon)$ is considered to originate from the asymmetric energy-dependent charge relaxation by the local Kondo scattering and multiple relaxation processes. In the present system, because the dispersive $\tau(\epsilon)$ seems to evolve near the critical region of the polar-nonpolar structural transition, its origin may be sought in the fluctuations or phase segregation in crystal structure. For Cu$_2$Se, for instance, a marked enhancement (by ~60%) of thermopower was observed during a continuous (second-order-like) structural transition, where critical scattering should be induced by fluctuation in crystal structure and density (35). Although the polar structural transition in pristine 1T'-MoTe$_2$ is of first order with minimal fluctuations, the transition is significantly smeared out when it is suppressed to low temperatures by the Nb substitution. Furthermore, considering the unusual decrease in SHG intensity below $T_S$ for $x = 0.08$, the polar phase on the verge of the critical composition might be subjected to strong fluctuation or phase separation with the nonpolar one at low temperatures. This would result in some critical scattering phenomena, causing an anomalous increase in $S$, as well as in $\rho_{yx}$ and $\rho_\nu$.

Note that the anomalous enhancement in $S$ is absent in the polar metallic state located away from the critical point. This is experimentally verified by measuring the thermopower for semimetallic W$_{1-x}$Ta$_x$Te$_2$ that keeps the polar orthorhombic structure in the whole investigated
range of temperature and Ta content (0 ≤ y ≤ 0.2). We observed no enhancement in S at low temperatures for this series of compounds, resulting in the S landscape being similar to that calculated for 1T'-Mo_{0.8}Nb_{1.2}Te_2 (Fig. 4C and fig. S5).

We here note that a small peak of thermopower is discernible around 30 K even for pristine x = 0, which is not reproduced by the calculation. Because the electron- and hole-like carriers coexist for x = 0, even a small change in compensation of thermopower by each carrier could result in its sign change and complex temperature variation, which is difficult to reproduce within the constant t approximation. As another origin of the small peak in thermopower for x = 0, we may be able to point out the contribution from the scattering by low-energy phonons activated in the polar phase (30, 31), the energies of which roughly correspond to the temperature range of the thermopower peak. However, because of the multiscatter effects, it is not practical to exactly explain this weak structure in thermopower.

The origin of the highly dispersive t(e) is still unclear and needs theoretical support. However, it may give us a clue that t(e) significantly differs between the polar and nonpolar phases. This is made clear by the scaling law on the magnetoresistance effect (the so-called Kohler’s law), which exhibits a substantial change across T_s (fig. S6). The fluctuation or mixing of the phases with different scattering processes might effectively yield a large gradient in t(e) (34).

The critical state of the polar-nonpolar transition thus provides a nice arena for enhancing the impact of polar order on transport properties by achieving the heterogeneous relaxation of charge carriers, which can be a promising means for designing novel thermoelectric materials. The x = 0.08 compound exhibits the peak of thermoelectric figure of merit ZT ~ 7.5 × 10^{-3} K^{-1} at ~40 K, where x is the thermal conductivity measured concomitantly with thermopower (see fig. S7, where the dimensionless figure of merit ZT is also plotted). This is comparable to the Z value for Na_{0.2}CoO_2 known for one of the best hole-type thermoelectric materials (Z ~ 1.6 × 10^{-3} K^{-1} at 40 K) (36). Below 20 K, the x = 0.08 compound even exceeds Na_{0.2}CoO_2 in Z value, indicating the potential for thermoelectric applications in the cryogenic region.

**MATERIALS AND METHODS**

**Crystal growth**

Single crystals of 1T'–Mo_{0.8}–Nb_{1.2}Te_2 were synthesized via a chemical vapor transport technique using iodine as a transport agent (14). Stoichiometric mixtures of Mo (99.9% purity), Nb (99.9% purity), and Te (99.999% purity) powders were sealed in an evacuated quartz tube (99.999% purity) and annealed down to room temperature to avoid the formation of the 2H phase with typical dimensions of 2 to 5 mm × 0.5 to 1 mm × 0.02 to 0.05 mm. The ampoule was equipped with a Saturn 70 CCD detector with MoKα radiation using an oscillation method. X-rays were monochromated and focused by a conventional mirror. The data were measured with an oscillation angle and a camera distance of 0.5° and 40 mm, respectively. The initial structure of the low-temperature phase was solved by a direct method using the program SHELXL-2014 (38).

**Electronic structure calculation**

Electronic structure calculations were performed within the context of density functional theory using the Perdew-Burke-Ernzerhof exchange-correlation functional modified by the Becke-Johnson potential, as implemented in the WIEN2k program (39). Relativistic effects, including spin-orbit coupling, were fully included. The muffin-tin radius of each atom R_{MT} was chosen such that its product with the maximum modulus of reciprocal vectors K_max becomes R_{MT}K_max = 7.0. The structural parameters were taken from the results of single-crystal structural analysis at 100 K for orthorhombic 1T'–MoTe_2 obtained in the present study (table S1). The corresponding Brillouin zone was sampled on an 8 × 16 × 4 k-mesh.

For the calculation of the Seebeck coefficient, we created an 88-band tight binding model using maximally localized Wannier functions (40–42). We chose valence p orbitals of Te and d orbitals of Mo as the projection centers of the Wannier functions. This model was then incorporated into the Boltzmann equation to calculate the Seebeck coefficient using a 50 × 50 × 30 k-mesh, where we assumed a constant
relaxation time for all the energy bands. The effects of Nb substitution were treated using the rigid band approximation, where the Fermi level was shifted down to an appropriate energy corresponding to the given hole concentration.

### SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/2/11/e1601378/DC1

### REFERENCES AND NOTES

1. P. W. Anderson, E. I. Blount. Symmetry considerations on martensitic transformations: “Ferroelectric” metals? *Phys. Rev. Lett.* **14**, 217–219 (1965).

2. S. S. Saxena, P. Monthoux. Superconductivity: Symmetry not required. *Phys. Rev. Lett.* **80**, 5766–5769 (1998).

3. D. Puggioni, J. M. Rondinelli. Designing a robustly metallic noncentrosymmetric ruthenate oxide with large thermopower anisotropy. *Nat. Commun.* **5**, 3432 (2014).

4. Y. Shi, Y. Guo, X. Wang, A. J. Princep, D. Khalyavin, P. Manuel, Y. Michiue, A. Sato, K. Tsuda, S. Yu, M. Arai, Y. Shirako, M. Akaogi, N. Wang, K. Yamaura, A. T. Boothroyd. A ferroelectric-like structural transition in a metal. *Nat. Mater.* **12**, 1024–1027 (2013).

5. H. Liu, Y. P. Du, Y. L. Xie, J.-M. Liu, C.-G. Duan, X. Wan. Metallic ferroelectricity induced by anisotropic unscreened Coulomb interaction in LiOsO₃. *Phys. Rev. B* **91**, 064104 (2015).

6. I. A. Sergienko, V. Keppeken, M. McGuire, R. Jin, He, S. H. Cumoe, B. C. Sales, P. Blaha, D. J. Singh, K. Schwarz, D. Mandrus. Metallic ferroelectricity in the pyrochlore Cd₂Re₂O₇. *Phys. Rev. Lett.* **92**, 065501 (2004).

7. T. Kolodziejczyk, M. Tachibana, H. Kawai, J. Hwang, E. Takayama-Muromachi. Persistence of ferroelectricity in BaTiO₃ through the insoluble-metal transition. *Phys. Rev. Lett.* **104**, 147602 (2010).

8. J. Fujikawa, A. Doi, D. Okuyama, D. Morikawa, T. Arima, K. N. Okada, Y. Keneko, T. Fukuda, H. Uchiyama, D. Ishikawa, A. Q. R. Baron, K. Kato, M. Takata, Y. Tokura. Ferroelectric-like metallic state in electron doped CaIrO₃. *Science* **335**, 532–533 (2015).

9. Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, M. S. Strano. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. *Nano. Technol.* **6**, 69–72 (2012).

10. M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, H. Zhang. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nat. Chem.* **5**, 263–275 (2013).

11. H. P. Hughes, R. F. Friend. Electrical resistivity anomaly in β-MoTe₂. *J. Phys. C Solid State Phys.* **1**, L103–L105 (1978).

12. M. B. Vellinga, R. de Jonge, C. Haas. Semiconductor to metal transition in MoTe₂. *J. Solid State Chem.* **2**, 299–302 (1970).

13. T. Zandt, H. Dwek, C. Janovský, R. Manzke. Quadratic temperature dependence up to 50 K of the resistivity of metallic Mo₂Te₅. *J. Alloys Comp.* **442**, 216–218 (2007).

14. K. Ikeura, H. Sakai, M. S. Bahramy, S. Ishiwata, Rich structural phase diagram and thermoelectric properties of tellurium-rich tellurides Mo₃NxTe₂. *APL Mater.* **3**, 041514 (2015).

15. S. Kabashima, Electrical properties of tungsten-ditelluride WTe₂. *J. Phys. Soc. Jpn.* **21**, 945–948 (1966).

16. M. N. Ali, J. Xiong, S. Flynn, J. Tao, Q. D. Gibson, L. M. Schoop, T. Liang. Haldolaarachige, M. Hirschberger, N. P. Ong, R. J. Cava. Large, non-saturating magnetoresistance in WTe₂. *Nature* **514**, 205–208 (2014).

17. D. H. Keum, S. Cho, J. H. Kim, D.-H. Choe, H.-J. Sung, M. Kan, H. Kang, J.-Y. Hwang, S.-W. Kim, H. Yang, K. J. Chang, Y. H. Lee. Bandgap opening in few-layered monoclinic MoTe₂. *Nat. Phys.* **11**, 482–486 (2015).

18. D. Kang, Y. Zhou, W. Yi, C. Yang, J. Guo, Y. Shi, S. Zhang, W. Cang, Z. Jiang, A. Li, K. Yang, Q. Wu, G. Zhang, L. Sun, Z. Zhao. Superconductivity emerging from a suppressed large magnetoresistive state in tungsten ditelluride. *Nat. Commun.* **6**, 7804 (2015).

19. X.-C. Pan, X. Chen, H. Liu, Y. Feng, Z. Wei, Y. Zhou, Z. Li, P. Yen, F. Song, X. Wan, Z. Yang, B. Wang, G. Wang, Y. Zhang. Pressure-driven dome-shaped superconductivity and electronic structural evolution in tungsten ditelluride. *Nat. Commun.* **6**, 7805 (2015).

20. Y. Qi, P. G. Naumov, M. N. Ali, C. R. Rajamathi, W. Schnelle, O. Barkalov, M. Hanfland, S.-C. Wu, C. Shekhar, Y. Sun, V. Süss, M. Schindt, U. Schwarz, E. Pippel, P. Werner, R. Hillebrand, T. Förster, E. Kampsert, S. Parkin, R. J. Cava, C. Felsing, B. Yan, S. A. Medvedev. Superconductivity in Weyl semimetal candidate MoTe₂. *Nat. Commun.* **7**, 11038 (2016).

21. A. A. Soluyanov, D. Gresch, Z. Wang, Q. Wu, M. Troyer, X. Dai, B. A. Bernevig. Type-II Weyl semimetals. *Nature* **527**, 495–498 (2015).

22. Y. Sun, S.-C. Wu, M. N. Ali, C. Felsing, B. Yan, Prediction of the Weyl semimetal in the orthorhombic MoTe₂. *Phys. Rev. B* **92**, 161107(R) (2015).

23. X. Qian, J. Liu, F. Li, J. Li. Quantum spin Hall effect in two-dimensional transition metal dichalcogenides. *Science* **346**, 1344–1347 (2014).

24. B. E. Brown. The crystal structures of WTe₂ and high temperature MoTe₂. *Acta Crystallogr.* **20**, 268–274 (1966).

25. W. G. Dawson, D. W. Bullet. Electronic structure and crystallography of MoTe₂ and WTe₂. *J. Phys. C Solid State Phys.* **20**, 6159–6174 (1987).

26. R. H. Dau, L. L. Xie, X. Zhang, R. J. Cava, Large, non-saturating magnetoresistant state in tungsten ditelluride. *Nat. Commun.* **6**, 7806 (2015).

27. M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, Y. Le Page. Computer derivation of the symmetry elements implied in a structure determination and refinement. *Acta Crystallogr.* **4**, 849–856 (1951).

28. I. Souza, N. Marzari, D. Vanderbilt. Maximally localized Wannier functions for entangled energy bands. *Phys. Rev. B* **76**, 035109 (2001).
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