Elastic and electronic tuning of magnetoresistance in MoTe₂

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Quasi–two-dimensional transition metal dichalcogenides exhibit dramatic properties that may transform electronic and photonic devices. We report on how the anomalously large magnetoresistance (MR) observed under high magnetic field in MoTe₂, a type II Weyl semimetal, can be reversibly controlled under tensile strain. The MR is enhanced by as much as ~30% at low temperatures and high magnetic fields when uniaxial strain is applied along the α crystallographic direction and reduced by about the same amount when strain is applied along the b direction. We show that the large in-plane electric anisotropy is coupled with the structural transition from the 1T’ monoclinic to the Td orthorhombic Weyl phase. A shift of the Td–1T’ phase boundary is achieved by minimal tensile strain. The sensitivity of the MR to tensile strain suggests the possibility of a nontrivial spin-orbital texture of the electron and hole pockets in the vicinity of Weyl points. Our ab initio calculations show a significant orbital mixing on the Fermi surface, which is modified by the tensile strains.

INTRODUCTION

Semiconducting transition metal dichalcogenides (TMDs) exhibit many versatile physical characteristics and have become a new paradigm for optoelectronic applications (1–11) based on exfoliated single-layer molecular structures (3–6). Fueled by intense interest on new device concepts, TMDs provide a platform from which optoelectronic properties such as spin-valley–coupled physics and two-dimensional valley excitons can be explored (12). They have a desirable optical band gap in the energy range of 1 to 2 eV, which is important for visible and near-infrared technologies. Manipulation of the band gap by reducing the sample thickness down to a monolayer or applications of strain can lead to distinct changes in their physical characteristics. As demonstrated in MoS₂ (6), the reduction in the number of layers leads to a shift of the valence band maximum from the center of the Brillouin zone closer to the edge, reducing the band gap as it aligns with the conduction band. Excitons (electron-hole pairs) are strongly bound in TMDs with binding energies of the order of 0.6 eV because of an enhanced electron-hole interaction, and when crystal thickness is reduced down to a monolayer, exciton binding energy is lowered. Similarly, the gap can also be reduced under tensile strain, leading to a transition to a metallic state.

Strain engineering is a widely used technique to control performance of electronic and spintronic devices (13) and has exposed a variety of strain-induced effects on the electronic behaviors including modulations of the band gap, carrier mobility, and light absorption. Many proposed devices reported in the literature make use of the application and control of compressive or tensile strain. Examples include a piezoelectric substrate for the application of biaxial compressive strain (13), flexible substrates such as polyethylene terephthalate films on a three-point apparatus (14), or flexible poly(methyl methacrylate) (PMMA) (ePlastics) for uniaxial tensile strain applications (15), and bending of polycarbonate beams using a four-point apparatus (16). Most studies have focused on the photoluminescence properties between the 2H and 1T’ phases. Little is known about the effects on the structural phase transition between 1T’ and Td and the magnetoresistance (MR) property. The observation of an extremely large MR (XMR) in the layered TMDs of WTe₂ and MoTe₂ has led to a surge of interest in this field (4), but the effects on MR due to strain have not yet been reported.

The layered crystal structure consists of strong in-plane covalent bonding and weaker van der Waals–type interactions between planes (17). In particular, MoTe₂ (18) can exist in several crystal configurations that include the hexagonal 2H, the metastable 1T’, and the low-temperature Td structures. β-MoTe₂ (1T’) can be stabilized by quenching and is metallic with a monoclinic (P2₁/m) structure (17–19). Mo is surrounded by Te in an octahedral environment, with Mo shifted off-center. It forms zigzag chains running along the a axis that distort the Te sheets, as shown in Fig. 1A, resulting in a tilted c axis with angle β ~ 93° (Fig. 1B). Upon cooling from room temperature, an anomaly appears in the transport data around 240 K that has been linked to a first-order structural transition from the 1T’ of β-MoTe₂ to the orthorhombic Td phase (Pmn₂₁) (Fig. 1B). The resistivity anomaly can be seen in Fig. 1C (measured along the b crystallographic direction) and is typical of what is found in the literature (18, 19). The resistivity shows metallic behavior with a thermal hysteresis setting in below room temperature. Because of the in-plane anisotropy, the resistivity along the a crystallographic direction is higher but shows the same essential feature (20). The Td phase exhibits the extreme MR effect and is the host of a Weyl semimetal state, a new state of matter in which collective excitations known as Weyl fermions may exist. Materials of this kind have unusual properties, where linear dispersions of the valence and conduction bands cross at Weyl points (21, 22). The band crossing is near the Fermi level, forming a gapless node (23). It has been suggested that the band structure of MoTe₂ is highly sensitive even to small changes in the lattice constants (23) either brought upon by strain or as a function of temperature.

Strain-modulated phase transitions have been studied in the TMDs especially in MoS₂. Using localized strain applied via wrinkling on atomically thin MoS₂ deposited on an elastomeric substrate, a reduction of the direct band gap was observed (24), presumably by shifting the conduction band. In MoTe₂, it was shown how the 2H–1T’ phases can be reversibly switched by strain, coupled with a semiconducting to metal transition (6). By introducing variable tensile strain, ε, through the application of an electric field on a piezoelectric stack, we show that an anisotropy develops in the MR that sets in with the symmetry breaking of the 1T’ and Td phases, resulting in different responses...
magnetic field dependence of the strain-induced change of MR measured the MR as a function of magnetic and tensile fields. The kink around 240 K is evidence of the structural phase transition from the 1T' to T_d phase.

\[ \beta = 93.4^\circ \]

At very thin, a different behavior was sometimes observed because of the strain effects. However, when the samples are rather typical of the samples that we measured. The two shown here is rather small (less than 0.05% at the maximum). This behavior is enhanced (Fig. 2D). The induced strain by the application of voltage perpendicular to the magnetic field shows strikingly different responses when the applied field is parallel or perpendicular to the structural transition, indicating that tensile strain along the c axis suppresses MR. When ε_a, the effect is reversed: The resistivity and consequently the MR are enhanced (Fig. 2D). The induced strain by the application of voltage is rather small (less than 0.05% at the maximum). This behavior is rather typical of the samples that we measured. The two shown here are representative of the strain effects. However, when the samples are very thin, a different behavior was sometimes observed because of the resistance dependence on ε at zero field. These results are reported in the Supplementary Materials.

To further characterize the changes in MR induced by ε, we measured the MR as a function of magnetic and tensile fields. The magnetic field dependence of the strain-induced change of MR (SMR), defined as SMR = MR(ε) - MR(ε = 0), is shown in Fig. 3. The SMR follows a near \((\mu_s H)^2\) behavior at all temperatures. It is negative when ε_b and positive when ε_a. Consistent with the results shown in Fig. 2, strain along the a direction enhances the MR; thus, SMR is positive. Similarly, when strain is applied along the b direction, the MR is reduced; hence, the SMR is negative. Moreover, with cooling, the strain effects become more pronounced, as can be seen from the temperature dependence of the data shown in Fig. 3 (A and B). In Fig. 3 (C and D), the SMR at 9 T is plotted as a function of ε for ε_b and ε_a, respectively. All curves exhibit a near-linear behavior, which is expected from the near-linear converse piezoelectric response of the piezoelectric material used to apply the tensile strain. The negative and positive SMR behavior is seen here as well.

In addition to the nonsaturated XMR, MoTe_2 exhibits a structural phase transition (1T' → T_d) near 240 K, evidenced by the kink in the resistivity as mentioned above. Strain has a direct effect on the structural transition as well. Figure 1 (C and D) shows the plots of the transport resistivity as a function of ε for ε_b and ε_a, respectively. Similar results were obtained with ε_a. Thermal hysteresis is seen on cooling and warming cycles in both crystallographic directions, as well as a shift in the structural transition temperature with the applied tensile field. The shift is best seen in the derivative plot, dp(T)/dT, of Fig. 1D. We define the maximum of dp(T)/dT as T_31 on cooling and T_32 on warming. T_31(ε = 0) - T_31(ε = 0) [T_32(ε = 0) - T_32(ε = 0)] follows a near-linear dependence on ε on cooling (warming) but shifts in the opposite direction depending on the crystallographic direction the strain is applied on (Fig. 1E). Furthermore, the strain-induced change of the width of the hysteresis loop is defined as HW(ε) - HW(0) = [T_32(ε) - T_32(ε = 0)] - [T_32(ε = 0) - T_32(ε = 0)]. When ε_b, the width grows, whereas it shrinks when ε_a, as seen in Fig. 1F. This suggests that the coexistence region of the 1T' - T_d phases is stretched in temperature when ε_b and compressed when ε_a. Therefore, upon cooling, the 1T' → T_d transition shifts down in temperature when ε_b and shifts up when ε_a. Similarly, on warming, the T_d → 1T' transition also shifts down in temperature when ε_b and shifts up when ε_a.
To understand how the Td phase of MoTe$_2$ responds to uniaxial strain, we performed ab initio calculations based on density functional theory (DFT), with spin-orbit coupling included (26, 27). Starting with the lattice constants obtained from the experiment, the lattice structure under uniaxial tensile strain is determined taking into account the anisotropic Poisson ratio $\gamma$ of MoTe$_2$. Our DFT calculation finds $\gamma_{ab} = 0.19$ and $\gamma_{ac} = 0.96$ for a tensile strain along the $a$ axis and $\gamma_{ba} = 0.31$ and $\gamma_{bc} = 0.54$ for a strain along the $b$ axis. Although these values agree on average with previous ab initio calculations assuming isotropic elastic constants (28), we emphasize that, similar to its electronic behaviors, MoTe$_2$ exhibits rather anisotropic elastic properties.

![Fig. 2. MR under field. (A and B) Schematic illustrations of the electric transport measurements with strain along $b$ and $a$ crystallographic directions, respectively. The red arrows indicate the expansion directions for the piezo stack under electric voltage. A ribbon-like MoTe$_2$ single crystal was glued to the surface of a piezo stack and cured so that it can transfer the strain effectively. Four gold wires were attached to the surface of the crystal for the four-probe electric transport measurements. Tensile strain was applied on MoTe$_2$ through a converse piezoelectric effect, which can be controlled by applying electric field on the piezo stack. (C and D) Plots of the in-plane resistivity at 3, 6, and 9 T as a function of strain.](http://advances.sciencemag.org/)
The band structures of the undeformed lattice and that under a 0.5% strain along a and b directions are shown in Fig. 4 (A to C). Modifications of the band dispersions are observed around the G point and along the Y → G direction, allowing a unique kind of band overlap manipulation through tensile strain application. In the case where strain is applied along the a axis, the band shifts give rise to a density of states (DOS) that is somewhat reduced around E_F. Conversely, if the strain is applied along b, the bands also shift up or down but in the opposite way (as shown in the figure), and the DOS appears to be enhanced at E_F. The opposite trends of DOS change under different strains are consistent with the observed enhanced and reduced SMR.

The k_z = 0 Fermi surface sheets in the vicinity of the Weyl points are shown in Fig. 4 (D to F) for the case of undeformed lattice, and that under uniaxial strains along a and b directions, respectively. The Fermi level has a more pronounced response to strain along the b direction. In particular, the small electron pocket close to the Weyl points disappears at the Fermi level at 0.5% strain in the calculation. Also shown along the contours is the orbital character (d versus p orbitals) of the corresponding Bloch states. Our DFT calculation reveals significant d-p orbital mixing at the Fermi level, indicating a nontrivial orbital pseudospin texture of the Fermi surface.

Although the DFT calculation provides an overall picture of how the band structures and Fermi surfaces are affected by strain, the relative change of the band parameters (of the order of 0.1 to 1%) seems too small to explain the large SMR observed in our experiments. For example, interpolating our calculation to the experimental value of 0.05% strain gives rise to a variation of band curvature of similar order. For a parabolic band, this variation indicates a similar 0.05% change in the electron effective mass, which is consistent with the observed less than 0.01% change in resistivity induced by strain at zero magnetic field. However, this band curvature variation seems too small to account for the observed 30% SMR, with an applied 0.05% strain. In DFT calculations, the changes in band parameters mainly result from strain-induced modification of orbital overlaps and hopping integrals. Below, we argue that the underlying mechanism of the large SMR is likely related to that of the XMR itself in MoTe_2, which involves enhanced electron scattering by the magnetic field.

The XMR phenomenon observed in MoTe_2 and a closely related compound, WTe_2, has been conventionally attributed to the perfect balance between the electron and hole populations (5, 29). This near-perfect compensation is crucial to the observed nonsaturating H^2 increase of MR within the framework of two-carrier model. However, the compensation effect itself does not explain the extraordinary magnitude of XMR. For example, it has been shown that reducing the sample thickness through exfoliation (30) significantly suppresses the XMR in WTe_2, whereas electron and hole remain perfectly compensated. Later, high-resolution angle-resolved photoemission spectroscopy (ARPES) and magnetotransport experiments (31, 32) also showed that the electron and hole densities are slightly imbalanced in WTe_2.

The underlying mechanism of XMR is likely due to a significant field-induced enhancement of electron backscattering (33). One scenario is that such backscattering is prohibited by symmetry at zero field, and the lifting of this protection by the magnetic field leads to the XMR. Microscopically, this protection could result from the nontrivial orbital and spin texture of the electron and hole pockets in proximity to a type II Weyl point. Recent observations of circular dichroism by ARPES confirm such spin-polarized Fermi surfaces in WTe_2 (34, 35).
Significant d-p orbital mixing, an important ingredient for nontrivial orbital angular momentum texture, is obtained from our DFT calculation for MoTe$_2$ (see Fig. 4). The electron and hole pockets inherit the chiral nature of the Weyl point and exhibit a definite helicity between their momentum and spin. Consequently, carrier scattering between pockets of opposite chiralities, especially those on the opposite sides of the F point, is suppressed because of the opposite sign of Berry phases from time-reversal-related scattering paths (36). In the presence of a magnetic field, the broken time-reversal symmetry leads to an imperfect cancellation of Berry phases and an enhanced interpocket backscattering (36).

Because orbitals directly couple to the lattice, applying strain to a Weyl semimetal is expected to modify the orbital texture of electron and hole pockets, hence affecting the inter-pocket electron scattering. Our DFT calculation shows that applying strains alters the orbital character of the electron and hole pockets (see Fig. 4, C and D). Here, we attribute the observed large SMR to the strain-induced modification of the pocket orbital texture, hence promoting or suppressing the inter-pocket backscattering. Recent theoretical studies have shown that elastic lattice deformations couple to the electronic degrees of freedom as pseudogauge fields in Weyl semimetals (37, 38). Moreover, because the tilting of the Dirac cone is along the a direction in MoTe$_2$, we expect rather different effects from tensile strains applied along a and b directions. Finally, we want to emphasize that the strain-induced pseudogauge fields preserve the time reversal symmetry, contrary to the real magnetic field. This explains the rather small strain-induced resistivity change at zero magnetic field. More precisely, the observed large SMR thus originates from a nontrivial interplay between the real and pseudogauge fields induced by magnetic field and strain, respectively. We hope that our experiments will motivate further theoretical investigations into this novel phenomenon.

MATERIALS AND METHODS

Sample synthesis

High-purity elements of Mo (99.9999%) and Te (99.9999%) were weighted and placed in a quartz tube, with a ratio of 1:2.5 for single crystal growth. The quartz tube was subsequently heated up to 1050°C and held for 24 hours. Then, the quartz tube was slowly cooled down to 900°C, followed by quenching into liquid nitrogen. Single crystals of MoTe$_2$ were grown from the Te flux.

Measurements

Single-crystal MoTe$_2$ was attached on the surface of a piezoelectric stack using ultrahigh-strength two-component epoxy glue (UHU). The epoxy glue was subsequently cured at 80°C by 1 hour. The sample and piezo stack were well electrically isolated because the epoxy glue is a very good insulator. Gold wires were then attached on the surface of MoTe$_2$, single crystal using silver epoxy. Silver epoxy was cured at 80°C by 1 hour. The sample was measured using a strain gauge, which was glued on the other side of the piezoelectric stack.

Calculations

We used DFT implemented in the Vienna Ab initio Simulation Package (VASP) for a material-specific calculation to study the uniaxial tensile strain effect of the T$_d$ phase of MoTe$_2$. VASP is a plane-wave–based projector-augmented wave pseudopotential method, with its exchange–correlation functional taking the generalized gradient approximation parameterized by Perdew–Burke–Ernzerhof. Specifically, ENCUT = 300 eV, K points = 12$^*6^*$3 generated with automatic k-mesh, and NBANDS = 128 with spin-orbital coupling switched on. The convergence in basis set and k-mesh size was verified. To simulate the effect of uniaxial tensile strain of this material, we started with the lattice constant obtained from experiment (a = 3.477 Å, b = 6.335 Å, c = 13.883 Å) and took its elastic property under full consideration. We used VASP to calculate its anisotropic Poisson ratios, $\gamma$, for uniaxial tensile strains and then applied these Poisson ratios to determine the corresponding lattice constants under 0.5% tensile strain along a and b axes. Specifically, our DFT calculation finds $\gamma_{ab} = 0.19$ and $\gamma_{ba} = 0.96$ along the a axis and $\gamma_{ab} = 0.31$ and $\gamma_{ba} = 0.54$ along the b axis. The electronic structure calculation was carried out on these more realistic lattice structures, and the evolution of the band structure and DOS under tensile strain is revealed. The Weyl points were checked to be consistent with previous publications and are indicated in Fig. 4 with filled dots. Wannier90 was used to fit the effective Kohn-Sham Hamiltonian on a very dense $k$-space mesh, and a homemade program mapped out the Fermi surface morphologies of the relevant structures at $k_z = 0$. These Fermi surface K points were compiled into a KPOINTS file for a second pass of VASP, which finally produces the mixed local p-d orbital ratio characters of the electron and hole pockets presented in the paper.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/12/eaao4949/DC1

fig. S1. XRD for MoTe$_2$ single crystal.
fig. S2. MoTe$_2$ crystal on the piezoelectric stack.
fig. S3. Transport and SMR data on samples 1 and 2.
fig. S4. Transport and SMR data on samples 3 and 4.
fig. S5. Conductivity, carrier density, and mobility with and without strain.
table S1. The voltage-strain relation of the piezoelectric stack.

REFERENCES AND NOTES


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Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

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