Pressure tuning of electronic transport properties of layered transition-metal dichalcogenides

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In many elements superconductivity appears under pressure. The goal of the ultra-high pressure group is to identify new superconductors. The electronic transport properties of two polymorphic phases of molybdenum ditelluride ($MoTe_2$) were studied at high pressures up to 40 GPa. The semiconducting α-phase (2H-$MoTe_2$) underwent an insulator to metal transition at pressure ≈16 GPa. No superconductivity was observed in this phase up to 40 GPa. β-$MoTe_2$ is metallic and superconducting over the entire pressure range studied. The critical temperature of superconductivity was found to be extremely sensitive to pressure in the low pressure range.

The layered transition-metal dichalcogenides TX_2 (about 60 in number) have been a matter of great research interest for several decades because of their wide range of electronic, optical, chemical, thermal, and catalytic properties of fundamental and technological importance. The family of layered TX_2 materials is structurally well-defined; the structure is formed by stacks of hexagonally packed planes in the sequence providing either the trigonal prismatic (e.g., MoS_2) or octahedral (e.g., HfS_2) coordination of metallic atoms. The electrical properties of these materials cover a wide spectrum from insulators (such as HfS_2) through semiconductors (such as MoS_2) to true metals (such as VSe_2). Many of these materials manifest charge-density waves (CDWs) and competition between CDWs and superconductivity. Some of the TX_2 materials (e.g., $TaTe_2$ and WTe_2) show structural distortions that make their properties very different than those of their undistorted analogues [1].

Molybdenum ditelluride ($MoTe_2$) is unique among the transition-metal dichalcogenides since it is the only material that can be grown in both forms: distorted and undistorted. Thermodynamically stable at ambient conditions is the undistorted α-$MoTe_2$, which is isostructural with hexagonal MoS_2 with trigonal prismatic coordination of Mo atoms (2H-phase). β-$MoTe_2$ is metastable at room temperature and has a more complex structure similar to that of WTe_2, in which the Mo atoms are octahedrally coordinated, but the metal atoms are shifted away from the center of the octahedron and make chains that run through the crystal. Electronically, α-$MoTe_2$ (2H-phase) is a semiconductor, whereas β-$MoTe_2$ (1T´-phase) shows metallic–like behavior and becomes superconducting at a critical temperature of 300 mK [2].

It is well known that pressure can effectively tune lattice structures and the corresponding electronic states in a systematic fashion, which avoids the complexity brought by chemical doping. Furthermore, as in the case of WTe_2, the Mo-4*d* and Te-5*p* orbitals are spatially extended, and, therefore, they are very sensitive to the application of external pressure. Here we report the study of electronic transport properties of $MoTe_2$ at quasi-hydrostatic pressures beyond 40 GPa.

To generate high pressures, we utilized a self-designed diamond anvil cell (DAC). The materials used to produce DAC and its dimensions allow electrical transport measurements at high pressures up to 100 GPa in a magnetic field with commercial PPMS and in a self-designed cryogenic setup in the temperature range of 1.5-300 K. The samples at high pressures were characterized by *in situ* Raman spectroscopy, which is known to be a powerful method to monitor pressure-induced phase transitions and (in combination with high-pressure synchrotron x-ray diffraction) to determine the structures of the new polymorph forms of matter. Raman spectroscopy studies were performed with a custom-designed Raman microscope system for DACs.

At pressures below 15 GPa, 2H-$MoTe_2$ remains semiconducting. At a further pressure increase to 16 GPa, 2H-$MoTe_2$ shows metallic–like behavior of the resistivity over the entire temperature range of 4-300 K. Thus, 2H-$MoTe_2$ undergoes an insulator-to-metal transition at ≈16 GPa in good agreement with recent theoretical predictions [3]. The pressure of metallization of 2H-$MoTe_2$ is significantly lower than that of the related isostructural 2H-MoS_2 (≈60 GPa) [4]. Furthermore, the metallization of MoS_2 is associated with an isostructural phase transition from $2H_c$ to $2H_a$ modification through layer sliding with a collapse of the *c*-lattice parameter and volume and also by changes in interlayer bonding [4]. Our high-pressure Raman spectroscopic studies indicate that this is not the case for 2H-$MoTe_2$. The initial $2H_c$ layer stacking remains stable up to at least 40 GPa, in

agreement with theoretical predictions [3]. 2H-$MoTe_2$ shows metallic-like behavior up to pressures of 40 GPa, and no signs of superconductivity have been found by cooling down to 1.5 K. It is of interest if the pressure-induced superconductivity in 2H-$MoTe_2$ can be observed at further pressure increases similar to MoS_2, in which superconductivity has been reported at ultrahigh pressures [5]. Corresponding electrical transport measurements in the megabar pressure range are underway.

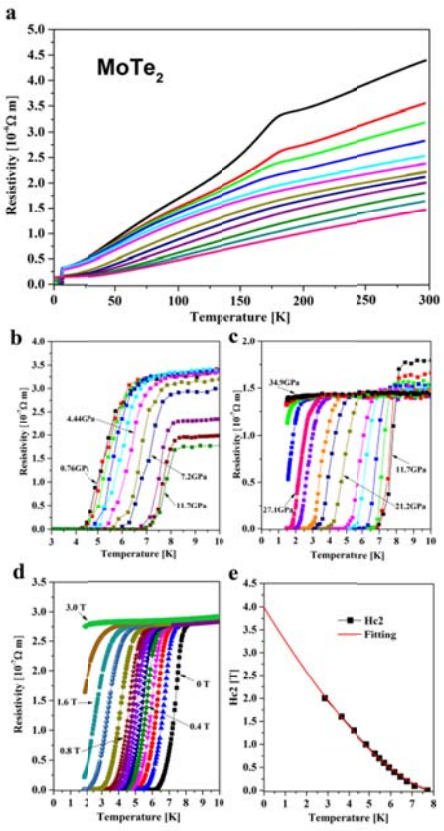

Fig. 1: Temperature dependence of electrical resistivity of 1T′-$MoTe_2$ at different pressures in the temperature range of 1.5-300 K (a) and at temperatures near the superconducting transition (b and c) without a magnetic field and at different magnetic fields at a pressure of 11.8 GPa (d). (e) The upper critical field analysis.

Measurements of the electrical resistivity of 1T´-$MoTe_2$ at temperatures down to 80 mK confirm its metallic-like behavior and superconductivity with T_c (onset) ≈300 mK, in agreement with literature data [2]. Upon application of pressures up to 40 GPa, 1T´-$MoTe_2$ remains metallic, and the resistivity continuously decreases as the pressure increases (Fig. 1). The superconducting T_c appears to be very sensitive to pressure. Already at pressure as low as 0.4 GPa, T_c increases dramatically to 4.9 K. T_c further increases with applied pressure, reaching its maximum value of 8.2 K at 11.7 GPa. Then, T_c gradually decreases, and, at pressures above 34.9 GPa, no superconducting behavior was observed down to 1.5 K (Fig. 2).

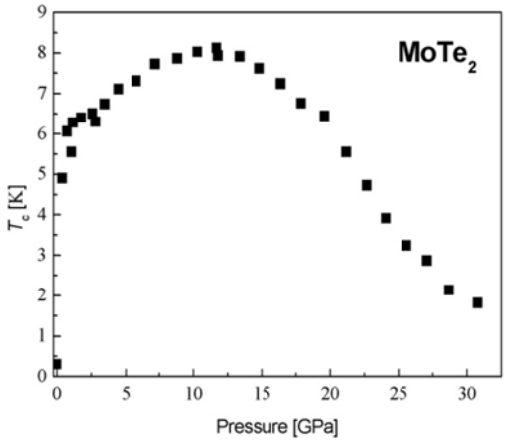

Fig. 2: The dome-shaped dependence of critical temperature of superconductivity of 1T′-$MoTe_2$.

The drastic increase in T_c in the low-pressure range as well as its decrease from the maximal value at higher pressures is not associated with structural transitions. The Raman spectra recorded at pressure increases up to the highest pressures contained only characteristics for 1T´ structure modes. The frequencies of both vibrational modes gradually increased without any discontinuities as the pressure increased, indicating normal mode behavior under compression. Strong pressure-induced enhancement of T_c has been observed in topological superconductors such as Bi_2Te_3 and Bi_2Se_3. The drastic increase in T_c at low pressures in $MoTe_2$ may be a manifestation of its topologically nontrivial electronic structure.

References

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