High-pressure studies of topological materials

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Transition-metal dichalcogenides (TMDs, TX_2), where T is a transition-metal cation and X a chalcogen anion, have attracted significant interest in the fields of chemistry, solid-state physics, and materials science over more than five decades due to their interesting structural chemistry, unusual electronic properties, rich intercalation chemistry, and wide range of potential applications. Recently, some TMDs have exhibited unusual properties originating from their nontrivial electronic structure topology. In this study, we applied high external (quasi)hydrostatic pressures up to 100 GPa to tune the lattice structures and correspondingly the electronic states of these materials in a systematic fashion. To study the effect of pressure on the structure and properties of the crystalline solid, Raman spectroscopy in combination with *in situ* synchrotron X-ray diffraction, electronic magnetotransport measurements (electrical conductivity, magnetoresistivity, and Hall effect), and DC magnetization measurements were used. With $MoTe_2$ and $PdSe_2$ we identified two compounds which combine topology with superconductivity. $MoTe_2$ with both superconductivity and a topologically non-trivial band structure is probably the first example of a time-reversal invariant topological (Weyl) superconductor. The unusual pressure dependence of superconductivity in pyrite-phase of $PdSe_2$ and topologically nontrivial bulk and surface states in its electronic structure offers a possibility to study the interplay between superconductivity and topological matter.

Layered TX_2 materials are structurally well-defined and form stacks of hexagonally packed planes providing either trigonal prismatic (e.g. MoS_2) or octahedral (e.g. HfS_2) metal coordination. The electric properties of these materials are diverse, ranging from insulators (HfS_2) to semiconductors (MoS_2) to true metals (VSe_2). Many of these materials manifest charge-density waves (CDWs) and competition exists between the CDWs and superconductivity. Some of the TX_2 materials such as $TaTe_2$ and WTe_2, show structural distortions that imbue very different properties compared to their undistorted analogues. Recently, WTe_2 with distorted orthorhombic structure has attracted significant attention due to its unusual electron transport properties originating from its topologically nontrivial electronic structure featuring a type-II Weyl-semimetal. The special electronic structure of topological Weyl-semimetals is the origin of intriguing electronic properties including chiral magnetic effects, negative magnetoresistance, and the quantum anomalous Hall effect.

In this study we explore the effect of pressure on the structure and electron transport properties of TMDs with different crystal and electronic structures displaying nontrivial topology. The results presented herein will lead to a deeper understanding of the interplay between crystalline structure, electronic properties, and superconductivity under high pressure in TMD materials. To obtain novel insights, we developed an experimental technique to allow the simultaneous study of structure, electron transport, and magnetic properties in an applied magnetic field.

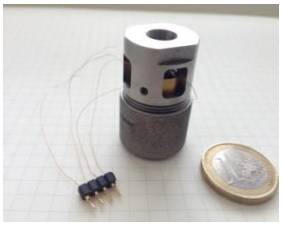

Fig.-1: Custom-designed miniature diamond anvil cell used for studies of structural, optical, magnetic, and electronic properties of materials at pressures up to 100 GPa.

Experimental technique development

Generation of static high external pressures

To generate a high external pressure up to 100 GPa we designed a custom miniature diamond anvil cell (DAC), which can be used to achieving (ultra-) high pressures (Fig. 1). Its miniature design fits inside the cryogenic setups of commercial PPMS, our custom-designed Raman spectrometer, Mössbauer spectrometer, and high-pressure dedicated beamlines of synchrotron radiation facilities such as ESRF, SPring8, NSRRC, and APS. The materials used to manufacture the cell and its design allow for use in magnetic fields up to 16 T at temperatures as low as 1.5 K at constant pressure.

Thus, the structural, optical, magnetic and electrical properties of the materials could be studied using a

single sample. This is important aspect different experimental environments often lead to contradictory results.

Raman spectroscopy to monitor phase transitions

The high sensitivity of elementary excitations in the solid materials to structural changes, phase transformations, [1] chemical reactions, magnetic, and electronic transitions [2] makes Raman spectroscopy useful for investigations of these effects under high pressure. These measurements should be combined with high-pressure synchrotron X-ray diffraction data when elucidating the structural features of novel high-pressure polymorphs. [1]

To perform high-pressure Raman spectroscopy, we designed a confocal Raman microscope with a laser excitation beam focused on a spot diameter of ~2– 3 μm. This facilitates the measurement of high-pressure Raman spectra with high spatial/spectral resolution and accuracy as well as for material characterization at the μm scale.

Electrical transport measurements

Electron transport experiments are essential for the study of electronic properties of matter under extreme conditions. Observations include interesting phenomena such as insulator-to-metal transitions, quantum critical phenomena, and pressure induced superconductivity. Despite significant progress in high-pressure experimental techniques, electrical transport experiments at very high pressures are "extremely difficult and remain the preserve of just a few talented experimentalists". [*S. Weir, in "High-Pressure Physics" ed. by J. Loveday (Chapman and Hall/CRC, 2012), p. 56*]. To perform high-pressure electrical transport measurements, we developed a technique based on the van der Pauw method allowing measurements of electrical resistivity and magnetotransport properties (magnetoresistivity and the Hall-effect) at pressures up to 100 GPa at 1.5–300 K and magnetic fields up to 9 T in commercial PPMS. The high-pressure transport experiments presented herein were used to explore the chemical, structural, and electronic parameters of a solid. These parameters lead to the appearance or enhancement of superconductivity with significant fundamental and technological impact. This technique is widely used to study the interplay between structure, magnetism, (using high-pressure Mössbauer spectroscopy with laboratory and synchrotron Mössbauer sources) and superconductivity in Fe-based superconductors and other related materials. [3]

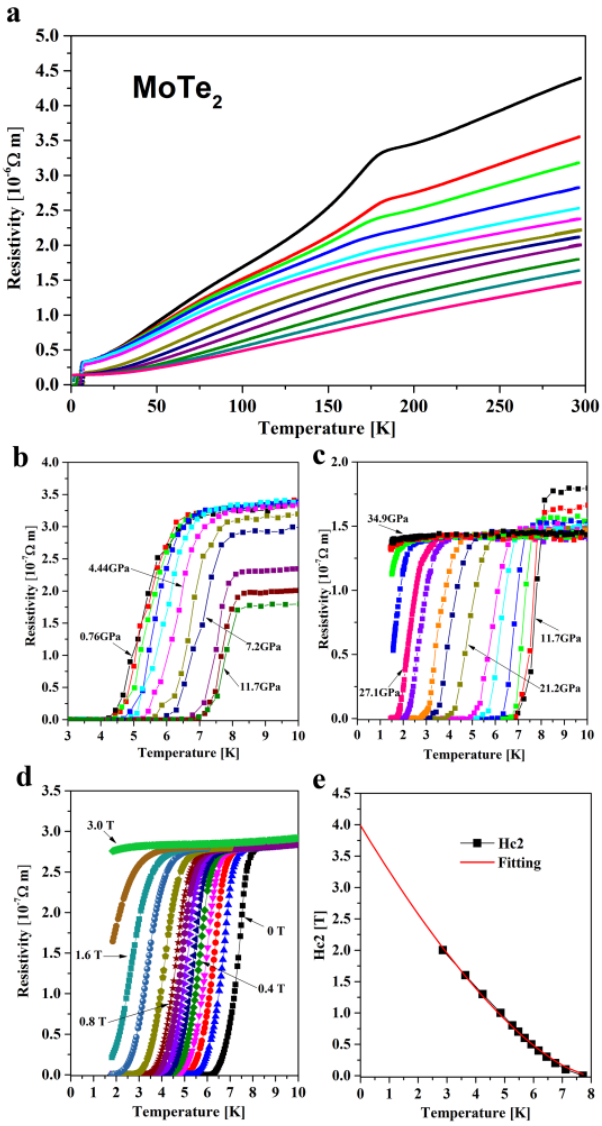

Fig.-2: Temperature dependence of the electrical resistivity of 1T´-MoTe2 at different pressures at 1.5- 300 K (a) and at temperatures near the superconducting transition (b and c) without a magnetic field and at different magnetic fields under 11.8 GPa of pressure (d). (e) The upper critical field analysis. [6].

$MoTe_2$ – a possible topological Weyl superconductor

Molybdenum ditelluride ($MoTe_2$) is unique among TMDs since it is the only material that can be grown in distorted and undistorted forms. The undistorted α-$MoTe_2$ is thermodynamically stable under ambient conditions and is isostructural with hexagonal MoS_2 with trigonal prismatic coordination of the Mo atoms (2H-phase). On the other hand, β-$MoTe_2$ is metastable at room temperature, and exhibits a more complex structure similar to that of the WTe_2 (WTe_2 has recently attracted significant attention as a type- II Weyl-

semimetal). In β-$MoTe_2$, the Mo atoms are octahedrally coordinated, but the metal atoms are shifted away from the centre of the octahedron and form chains that run through the crystal.

Electronically, α-$MoTe_2$ (2H-phase) is a semiconductor, whereas β-$MoTe_2$ (1T´-phase) shows metallic-like behaviour. Calculations of their electronic structures showed that β-$MoTe_2$ is also a type II Weyl-semimetal. [4] This theoretical prediction was subsequently confirmed by the experimental observation of Fermi arcs. [5] Our electrical resistivity measurements indicate that the Weyl semimetal T_d- MoTe2 becomes superconducting below 0.3 K. [6] Thus, T_d-$MoTe_2$ is a rare example of a material with both superconductivity and topologically nontrivial band structure. Further studies showed that the critical temperature of superconductivity, T_c, in $MoTe_2$ and the width of the superconducting transition are sensitive to doping, indicating unconventional superconductivity in T_d-$MoTe_2$.

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

Application of external pressure to β-$MoTe_2$ dramatically influences its T_c (Fig. 3). [6] Upon application of pressures up to 40 GPa 1T´-$MoTe_2$ remains metallic and its resistivity continuously decreases with increasing pressure (Fig. 2). The superconducting T_c was quite sensitive to pressure. At pressures as low as 0.4 GPa, the T_c increases dramatically to 4.9 K and further increases with applied pressure reaching a maximum value of 8.2 K at 11.7 GPa. The T_c gradually decreased with further pressures increases and at 34.9 GPa no superconducting behaviour was observed at 1.5 K. (Fig. 3)

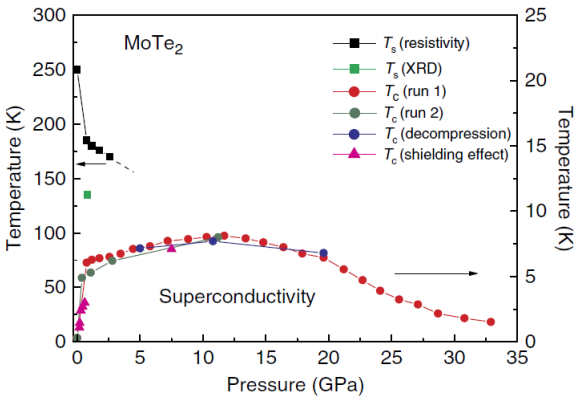

Fig.-3: Electronic phase diagram of β-MoTe2. [6]

The superconducting behaviour of the material in the low-pressure region clearly differs from that at high pressures. At low pressure, the sharp increase in T_c is concomitant with the strong suppression of the structural transition between low-temperature orthorhombic T_d structure and its topologically trivial monoclinic distortion denoted as its T' structure (structural transition temperature at ambient pressure, T_s=260 K, Fig. 3). This is similar to observations for other superconductors with various competing phase transitions. A drastic increase in the T_c occurs within the T_d phase, which was shown by DFT calculations to be a Weyl semimetal with band structure around the Fermi level, which is extremely sensitive to changes in the lattice constants. Thus, it is expected that dramatic structural and electronic instabilities would emerge in the low-pressure region, accounting for the strong enhancement of T_c. It should be noted that the pressure induced enhancement of T_c is also observed in topological superconductors such as Bi_2Te_3 and Bi_2Se_3. The drastic increase of T_c at low pressures in $MoTe_2$ is likely a manifestation of its topologically nontrivial electronic structure.

This observation attracted significant research interest and many subsequent studies have been devoted to understanding the properties of the β-$MoTe_2$. Recently, high-pressure muon-spin rotation experiments probing the temperature-dependent magnetic penetration depth in T_d-$MoTe_2$ were reported. The superconducting order parameter in T_d-$MoTe_2$ was determined to exhibit 2- gap s-wave symmetry. Considering the strong disorder suppression of T_c in $MoTe_2$, it was suggested that the topologically nontrivial s^{+-} state is more likely to be realized in $MoTe_2$, making β-$MoTe_2$ the first example of a time-reversed invariant topological (Weyl) superconductor. [*Z. Guguchia et al., Nat. Commun.* ***8*** *(2017) 1082*] Recent studies have also demonstrated the possibility to independently control the inversion symmetry breaking via structural manipulation and superconductivity in $MoTe_2$ by adjusting temperature, hydrostatic pressure, and non-hydrostatic pressure component symmetry (uniaxial-like stress). This offers a possible route for the development of a superconducting system with strain tunable Weyl Fermi arcs and nontrivial band topology. [*C. Heikes et al., arXiv:1804.09093v1*]

Evolution of WTe_2 charge carriers at the transition in the superconducting state: Hall-effect measurements

The exploration of the chemical, structural, and electronic parameters of a solid which influence the appearance or enhancement of superconductivity is a subject of intensive research. The application of external pressure is can be used to continuously tune the crystal and electronic structures of solid and elucidate their interplay.

In the type-II Weyl semimetal WTe_2, superconductivity can be induced by applying external pressure. Superconductivity in WTe_2 emerges from a suppressed large magnetoresistant state originating from a special electronic band structure with multiple electron and hole pockets at the Fermi-level. To obtain further insight into the interplay between the electronic structure and superconductivity in WTe_2, we performed Hall-effect measurements at different pressures (Fig. 4).

Measurements were performed on single crystalline samples with electrodes attached to the sample in a van der Pauw geometry in commercial PPMS using the field sweep technique.

Application of high pressures leads to suppression of the large magnetoresistant state in agreement with the literature. Analysis of the Hall resistivity with the two-band model revealed an increase in carrier densities with a simultaneous decrease of their mobility with increasing pressure. Remarkably, the Hall coefficient changes its sign at approximately 5 GPa (Fig. 4a) and the superconducting state emerges (Fig. 4b). Thus, the emergence of superconductivity in WTe_2 at high pressures is associated with a drastic reconstruction of the Fermi-surface. Further studies are required to elucidate the origin of superconductivity in WTe_2.

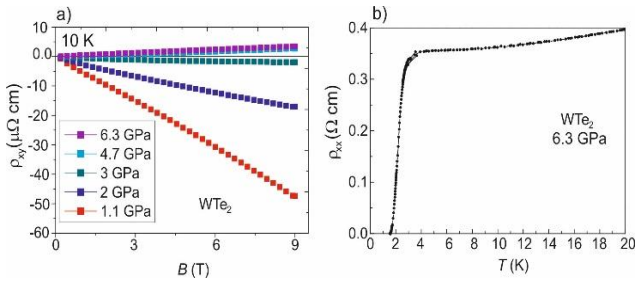

Fig.-4: Hall resistivity of WTe2 at 10 K at different pressures (a). At pressures near 5 GPa, the Hall coefficient changes sign (a) and superconductivity is observed (b).

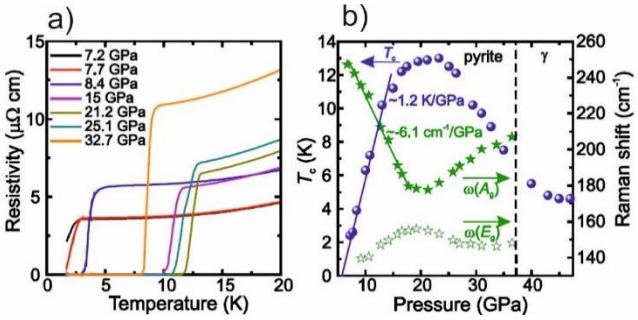

Fig.-5: (a) Superconductivity emerges in pyrite-PdSe2 at the Tc (b) exhibiting a dome-shaped dependence on pressure in correlation with the pressure evolution of the frequencies of the internal stretching vibration (Ag mode) and vibrational (Eg mode) modes of the Se2 dumbbells [7].

Superconductivity in the pyrite-phase of $PdSe_2$

The non-layered 3D structures of the late TMDs (groups VII and beyond) show interesting insulator-metal transitions with particular attention paid to the TMDs with a pyrite structure. These materials exhibit various magnetic and electrical phenomena which range from the prototypical antiferromagnetic Mott insulator NiS_2 to superconducting copper dichalcogenides. Typical pyrite structure features a strong pairing of the chalcogen atoms (X) forming $(X–X)^{-2}$ dimers. The bond length of these pairs is considered to be a key parameter controlling the critical temperature of superconductivity in the defective pyrite compounds Ir_xSe_2 and $Ir_{0.94-x}Rh_xSe_2$.

Pd-compounds, such as PdS_2 and $PdSe_2$, are particularly interesting materials for the study of the interplay between structure, bonding, and electronic properties as they feature unique crystal structures which are hybrids between 2D and 3D structures.

The application of pressure systematically changes the transport properties of $PdSe_2$, leading to pressure-induced metallization at ~3 GPa within the ambient pressure PdS_2-type structure. Interestingly, a superconducting state emerges upon structural transition to the pyrite phase above 6 GPa (Fig. 5a). The T_c increases rapidly with increasing pressure and reaches a maximum of 13.1 K at ~23 GPa, which is the highest T_c reported in TMDs to date. [7] Figure 5b shows a clear correlation between the pressure dependence of T_c and the frequencies of the A_g and E_g modes which directly reflect the strengths of the Se-Se and Pd-Se bonds in $PdSe_2$, respectively. Thus, T_c rapidly increases with weakening of the Se-Se bonds due to charge transfer from the metal to the antibonding states of the Se_2 dumbbell, effectively oxidizing Pd (d^8 to $d^{8-\delta}$).

The large family of transition-metal compounds with pyrite structure offers a wide range of possibilities for tuning the metal oxidation state and bonding strength of the dumbbells by chemical substitution. This represent an opportunity to achieve higher values of T_c and eventually stabilize the superconducting state at ambient pressure.

The *ab initio* electronic band structure calculation results indicate the presence of Dirac and nodal-line fermions in the vicinity of the Fermi energy level [7]. These fermions are protected by the pyrite structure symmetry [8], resulting in interesting superconducting states. However, the ultimate significance of the topologically nontrivial electronic states for superconductivity in the pyrite phase of $PdSe_2$ remains to be proven. Nevertheless, the topological nontrivial bulk and surface states have attracted significant interest in context of their interplay with superconducting instability.

Conclusions

High-pressure studies of TMDs with topologically nontrivial electronic band structures highlight the applicability of high pressure for tuning the crystalline and electronic structures of solids to elucidate their mutual dependence. The presence of topologically nontrivial bands allows for the probing of the interplay between topological states and superconductivity. This can lead to the development of various exotic superconducting states. The apparatus and complementary techniques developed in our laboratory allow the simultaneous study of structural and electronic (as well as magnetic in relevant cases) properties as a function of applied external pressure on a single sample. This enables the investigation of the interplay between superconductivity and topological matter.

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