The pressure-dependence of the band gap of tellurium

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Abstract. Elemental tellurium is a semiconductor with a small band gap of around 330 meV. Under the application of hydrostatic pressure, the band gap narrows, and it has been suggested that below its crystal phase transition at 40 kbar, the gap might close, leading to a transition into a topologically non-trivial state. Here, we present a pressure dependent study of the gap size of tellurium up to 22kbar, studied by temperature dependent electrical transport. We identify the gap size to be still well above 100 meV at our maximum pressure. Extrapolation of our data, assuming a non-linear gap narrowing (in agreement with previous studies), leaves us to assume that the gap does not close within the ambient pressure crystal phase. However, when assuming a linear narrowing of the gap, we leave a small possibility that there exists a minor pressure window at which a topological phase transition could occur. Furthermore, as the second systematic study of the gap size via transport, we see that historical inconsistencies between the measured gap size via transport and the measured optical gap size seem to be systematic and probably reflect some deeper physics of the material.

1. Introduction

Elemental tellurium at ambient pressure is a semiconductor with a relatively small band gap between 330 and 350 meV. The band gap is almost direct and centred around the H-point, where the top of the valence- and the bottom of the conduction band display a camel-back like double maximum (or minimum, respectively) [1,2].

Tellurium’s crystal structure at ambient pressure (named Te I within this paper) is quite unique in the sense that it consists of helices of tellurium atoms, which are arranged in a hexagonal lattice (see fig. 1). The intrahelix bonds are of covalent type, while the interhelix bonds are van-der-Walls like. This leads to anisotropy in almost all physical quantities [3-6]. The application of hydrostatic pressure causes a narrowing of the distance between the helices, while the helices themselves straighten, effectively increasing the distance of atoms within the same helix [7].

At 40 kbar, tellurium displays a crystal phase transition to the Te II phase [8]. Further, it was shown in 1974 that the band gap narrows under the application of modest hydrostatic pressure up to 7 kbar [9]. Within this study, Koma et. al. had observed a non-linear pressure dependence from their conductance and Hall data, which suggested that the gap does not close before the crystal phase transition at 40 kbar. This hint to the inexistence of a metallic Te I phase has been supported by optical gap measurements by Anzin et. al. up to 10 kbar [10] and by a LASER emission study of Pine...
et. al. with a nominal maximum pressure of 8 kbar [11]. These three systematic studies of the band gap size under modest hydrostatic pressure agree on the non-linearity of the gap narrowing, but they do show strong deviations in term of the exact band gap size, as will be discussed further below.

Two independent theoretical studies [12,13] from the last decade suggested that a gap closing within the Te I phase would be highly interesting, as it might lead to topological non-trivial phases. The strong spin-orbit coupling in the material, makes tellurium an interesting element to study in theory, when searching for topologically non-trivial states of matter. In 2013, Agapito et. al., based on their density functional theory (DFT) calculations, suggested that the gap might close around 20 kbar, where tellurium might become a specific type of topological insulator [12], while Hirayama et. al. proposed, it might become a Weyl semimetal [13]. However, one should mention that the interplay of weak van-der Waals forces and covalent bonds makes accurate band calculations from DFT specifically challenging.

Up to very recently, measurements in the pressure range between 10 and 40 kbar, still below the crystal phase transition, only were realized by Shchennikov in 2000 [14] and he, too, did not find any indication of a pressure induced gap closing within the Te I phase.

Now, a recent experimental study has been interpreted in a manner, which contradicts the previously mentioned experimental results and the authors interpret their data in favor of a possible gap closing with an emergent Weyl semimetal phase [15].

Here, we present an experimental study of the energy gap via transport measurements up to 22 kbar. Our data agree well with the seminal study of Koma et. al., which used the same method. However, as we will point out below, both seminal optical studies match also well between themselves. Therefore, we suggest that there is some real physics behind the discrepancy of the two methods.

Further, if we assume, contrary to the general believe, a linear gap narrowing, our data suggests that there may exist a small pressure window at which Te I becomes metallic.

2. Experiment
Transport measurements have been performed on a high-quality single crystal with 99.9999% chemical purity, purchased from Princeton Scientific™. Sample size is $3 \times 1 \times 0.5$ mm. The sample has been carefully cleaned with ethanol and, subsequently, contacts for standard 4-wire technique have been attached with Sigma Aldrich™ silver paint using 25 µm platinum wires.
The direction of the electrical current is perpendicular to the c-axis (the screw axis of the helices as displayed in fig. 1a). The sample was installed in a hydrostatic piston cylinder pressure cell with a 1:1 mixture of Fluorinert™ FC77/FC70 as the pressure transferring medium. As a low temperature pressure gauge, we used a piece of lead and monitored the development of the superconducting transition. Simultaneously, a manganin wire, installed within the cell, was used to estimate the applied pressure at room temperature. The cell was slowly cooled from room temperature, using two different adiabatic demagnetization refrigerators (ADRs) with base temperatures of 50 mK (at CBPF in Rio de Janeiro) and 250 mK (at the Cavendish Laboratory in Cambridge), respectively. Within this proceedings paper, we only focus on the high temperature range. In another publication, currently under consideration for publication in Nature Communications, we discuss the low temperature and magnetoresistance behaviour of the same sample.

Both used ADRs possess three different cooling stages. The first one cools the sample down to liquid helium temperature with thermal contact via exchange gas within an inner vacuum chamber (IVC). The second one is via a 1 K stage, working via pumping, and the third one is the actual ADR. As we were interested in the resistivity at relatively high temperatures, we got to liquid helium temperature without any exchange gas in the IVC. This way, the sample stage is cooled via the 1 K stage, which is connected to the Helium bath via a copper rod. Using this method, the cooling from room temperature to 4 K took about 24 hours for each pressure point. This allowed the proper acquisition of reliable data at these relatively high temperatures.

**Figure 2. a)** Resistivity curves of tellurium under pressure. The resistivity axis is logarithmic. The temperature axis goes with $1/T$. The dashed lines correspond to the intrinsic behaviour in the high temperature limit. b) The extracted values for the gap size $\Delta$ over pressure (blue circles). Our polynomial fit, a forced linear fit and the fits from historical publications are displayed for comparison.

### 3. Results & Conclusion

Fig. 2 a) shows the temperature dependent resistivity $\rho(T)$ curves plotted as $\ln \rho$ vs. $1/T$. Since the resistance of semiconductors at relatively high temperatures generally behaves in an intrinsic manner, it follows

$$\rho(T) \propto e^{\frac{\Delta}{k_B T}}$$

with $\Delta$ being the band gap size and $k_B \approx 86.1733\ldots \mu$eV/K the Boltzmann constant. At lower temperatures, the transport is dominated by different processes due to the natural occurrence of vacancies, which serve as acceptors, in tellurium. Thus, the slope of the curve approximating the high
temperature limit at room temperature around 300 K (marked by the dashed lines in fig. 2a), allows a
decent estimation of the real band gap size. This is plotted in fig. 2b) over the pressure $P$ together with
five curves to compare.

Like previous experimental studies, our data also suggests a non-linear narrowing of the gap.
However, we still performed a forced linear fit, as one might argue that the data might be considered
ambivalent. The fit is shown in the figure and exhibits a respective function of the gap size,
\[
\Delta_{\text{linear}}(P) = 340 \text{ meV} - 9.28 \frac{\text{meV}}{\text{kbar}} \cdot P.
\]

We can see in that this linear fit does not reproduce the data very well. However, in a scenario, in
which the gap closes linearly, it seems as if there could exist a small window in which Te I is metallic
below 40 kbar.

Naturally, a much better fit is given by the polynomial one,
\[
\Delta_{\text{polynomial}}(P) = 344 \text{ meV} - 13.35 \frac{\text{meV}}{\text{kbar}} \cdot P + 0.22 \frac{\text{meV}}{\text{kbar}^2} \cdot P^2.
\]

As can be seen in the figure, this function agrees very well with the gap closing function of Koma
et. al., which has been determined using the same method based on data of a smaller pressure window.
Of course, we do not think that the gap function follows exactly the polynomial for higher pressures (it
just gives a good approximation up to 22 kbar). We deem it likely that the non-linearity emerges from
the anisotropy of the material, which naturally lowers, when approaching higher pressures. Thus, one
might expect that, for example, between 30 and 40 kbar, the gap closing function is more linear.

However, in the same figure, it is apparent that, while the two optically measured curves by Anzin
and Pine agree well among each other in the low pressure range (which is the range in which data
points were acquired), they do not agree at all with our and Koma’s study. This is specifically
interesting, when acknowledging that at 8 kbar, (a value that is still in the range of data points within
these studies), the difference accounts for astonishing ~50 meV. Of course, we can only speculate
about the origin of this impressive difference, but it might be related to the unusual thermal expansion
anisotropy in tellurium, as the optical measurements were all performed at 300 K, while the resistivity
curves are acquired over a wide temperature range in which the real band gap actually might change
due to the change of the lattice parameters in different directions.

In conclusion, we deem it very unlikely that a topological phase transition can be induced into Te I
by applying hydrostatic pressure. However, we see that the gap closing occurs in a manner that is very
consistent with seminal studies, which took advantage of the same experimental method. But we
clearly see a systematic deviation to historical studies that have been performed using optics. This
might very well be related to the peculiar and non-trivial physics of elemental tellurium.

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