



## Anisotropic transport properties of tungsten disulfide



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### ABSTRACT

Single crystals of WS<sub>2</sub> were prepared by chemical vapor transport method using sulfur as a transport agent. Measurements of electrical resistivity, Seebeck coefficient and thermal conductivity as a function of temperature, along the in-plane and the out-of-plane directions reveal distinct trends. In our interpretation these differences are mainly due to the different nature of the chemical bonding in the two directions and to the presence of impurity intercalates in between the planes.

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Transition metal dichalcogenides (TMDs) are attractive two-dimensional materials displaying a variety of physical properties and ground-states. In the past, members of the family presenting charge-density wave order [1] and superconductivity [2,3] have been studied extensively. Recently, since bulk TMD crystals can be exfoliated down to a single-layer (or the layers can be grown from vapor phase), even simple semiconductors started to be investigated in view of electronic and photonic applications like field-effect transistors [4], light emitting transistors [5], photodetectors [6], photovoltaics [7], photoelectrochemical cells [8] and valleytronic devices [9], just to mention a few. WS<sub>2</sub> is one of the most studied compounds belonging to this class of materials. It is preferentially used in heterostructures, e.g. with graphene, because of its strong spin-orbit coupling [10]. It crystallizes in a layered structure where each W atom is surrounded by six sulfur atoms in a trigonal prismatic configuration. Although some recent works investigated the electrical properties of thin films [11] and single-layer [12] tungsten disulfide, an exhaustive and systematic study of the anisotropy of electrical and thermal properties of bulk crystals is still missing. These, however, are important for large-scale thin film devices assembled from exfoliated samples as reported in Ref. [8], where conduction across the film is likely to be limited by transport perpendicular to the layers. Here, we report a detailed description of resistivity, thermoelectric power and thermal conductivity of WS<sub>2</sub> single crystals grown by chemical vapor transport (CVT) method. These transport coefficients were measured in the 4–300 K temperature range

along the two principal crystallographic directions: perpendicular and parallel to the WS<sub>2</sub> planes. The details concerning the procedure and the experimental set-up used for resistivity, Seebeck coefficient and thermal conductivity measurements are described in references [13, 14,15] respectively. In order to measure the out-of-plane Seebeck coefficient and thermal conductivity, different crystals were carefully piled to form a stacked structure. Silver glue from DuPont was used to ensure good mechanical stability and thermal contact between the different crystals. The contribution of the silver glue to the WS<sub>2</sub> Seebeck coefficient was negligible. To prove the validity of our method we measured the room-temperature out-of-plane thermal conductivity of an individual single crystal of WS<sub>2</sub> employing a  $3\omega$ -method as described elsewhere [16]. The value resulting from the  $3\omega$ -method (1.1 W/mK), was in good agreement with what we obtained employing the steady-state method.

Contrary to what was observed for single-layer TMDs where the surrounding environment can deeply affect the performances and the properties of the material under investigation [12], single crystals of TMDs display a very good chemical and physical stability allowing a reliable analysis of their characteristics. However, we recently demonstrated that in MoS<sub>2</sub> the different transport agents (I<sub>2</sub>, Br<sub>2</sub>, TeCl<sub>4</sub>) employed during the CVT growth can be incorporated in the crystal and can affect the transport properties of the material [13] by introducing some doping. The WS<sub>2</sub> samples studied in this work were obtained using sulfur as a transport agent and therefore we do not expect any significant contamination by the transport agent molecules, although other impurities present in the starting materials for synthesis (see below) and vacancies, interstitials can influence the electronic

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properties. Stoichiometric amounts of tungsten wires and sulfur powder were encapsulated with the transport agent in a quartz ampoule. The sealed ampoule was placed in a two-zone furnace first at constant temperature (i.e. 900 °C) for the synthesis of WS<sub>2</sub> powder. The single crystals were grown subsequently by CVT according to the conditions described in Ref. [17]. In order to check the quality of the crystals, we performed in-beam activation analysis (IBAA) [18]. The results, summarized in Table 1, indicate a WS<sub>1.868</sub> stoichiometry with a relative error of approximately 10%, thus we conclude that the samples are close to the nominal composition. The minute amount of other elements is probably caused by impurities present in the starting materials. Small departure from the stoichiometry, and the impurities may cause doping of the crystals.

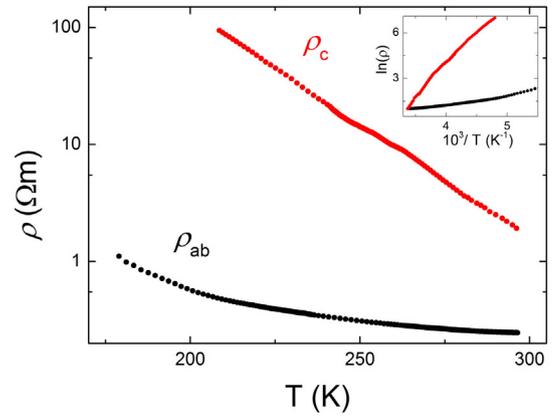
Electrical resistivity was measured along the WS<sub>2</sub> plane ( $\rho_{ab}$ ) and perpendicular to it ( $\rho_c$ ). The results are presented in Fig. 1. The value of  $\rho_{ab}(300\text{ K}) = 0.24\ \Omega\text{m}$  is in good agreement with that reported by other authors [19,20]. The electronic anisotropy is  $\rho_c/\rho_{ab} \sim 8$  at 300 K and it increases with lowering temperature similarly to what was observed in MoS<sub>2</sub> [13]. However, the resistivity anisotropy in our WS<sub>2</sub> samples is considerably smaller than in MoS<sub>2</sub>. Both  $\rho_{ab}$  and  $\rho_c$  follow a thermally activated temperature dependence of the form  $\rho_0 \exp(\Delta/k_B T)$  (where  $k_B$  is the Boltzmann constant, and  $\rho_0$  a temperature independent factor).  $\Delta$  is not the 1.4 eV bandgap [17] of WS<sub>2</sub> as already observed by spectroscopic techniques by other groups [19, 20] but it corresponds to low lying impurity levels. The inset in Fig. 1 shows the Arrhenius plot for  $\rho_{ab}$  and  $\rho_c$ . The in-plane activation energy ( $\Delta_{ab} = 40\text{ meV}$ ) is 6 times lower than the out-of-plane value ( $\Delta_c = 230\text{ meV}$ ). The higher activation for the interplane transport is a striking result and it seems to be general since a similar effect was observed for MoS<sub>2</sub> [13]. The simple model proposed in Ref. [13] is the following. Because of the larger distance between W atoms along the  $c$  direction the overlap integral is more sensitive to perturbation such as intercalates in the Van der Waals gap. As a consequence, the electronic transport between the planes picks up a phonon-mediated hopping character with an additional activation energy with respect to in-plane transport. This results in a higher energy barrier for charge moving along the  $c$ -axis compared to charge moving in the  $ab$  plane. This significant difference between the measured  $\Delta_{ab}$  and  $\Delta_c$  in WS<sub>2</sub> is particularly interesting, it could be relevant in hetero-structures as well, and it should be properly addressed by suitable theoretical models.

Thermoelectric power or Seebeck coefficient ( $S$ ) was also measured along the two crystallographic directions. A temperature gradient was applied across the sample while the voltage was measured in the same direction. Fig. 2 shows  $S$  measured along the WS<sub>2</sub> plane ( $S_{ab}$ ) and perpendicular to it ( $S_c$ ). The measurement of  $S$  at very low temperature was precluded by the high sample resistance. The positive sign of both  $S_{ab}$  and  $S_c$  at room temperature suggest that mainly acceptor levels (hole-like carriers) contribute to the charge transport. This corroborates earlier reports [11,21] for in-plane measurements. However the change of sign in  $S_{ab}$  around 200 K indicates the presence of both acceptor and donor levels within the WS<sub>2</sub> bandgap. The high values of

**Table 1**

Summary of the molar percentages (mol%) and their relative uncertainty (unc%) of elements found by neutron IBAA analysis in CVT grown WS<sub>2</sub> single crystals. The minute amount of external elements is probably caused by impurities present in the starting materials.

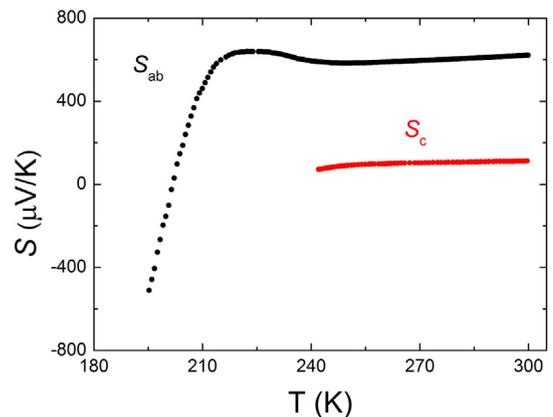
Element	mol%	uncertainty%
S	64.9	1.1
W	34.7	3
B	0.06	2.6
Cl	0.08	4
Cd	0.005	6
In	0.009	3.2
Na	0.28	3.2



**Fig. 1.** Temperature dependence of the in-plane (black curve) and out-of-plane (red curve) resistivities of WS<sub>2</sub> single crystals. The inset shows the Arrhenius plot of the two resistivities. The difference in slopes is due to phonon-mediated charge transfer along the  $c$  directions that requires a higher activation energy than in the  $ab$  direction.

$S_{ab}(300\text{ K}) = 620\ \mu\text{V/K}$  and  $S_c(300\text{ K}) = 112\ \mu\text{V/K}$  is characteristic of non-degenerate semiconductors but their temperature dependences significantly differ from the expected  $S \propto 1/T$  behavior [22]. We instead observe a nearly temperature-independent Seebeck coefficient down to 240 K that can be ascribed to polaronic charge carriers as explained for other materials such as TiO<sub>2</sub> [23], MoS<sub>2</sub> [13] and boron carbide [24]. In this scenario  $S$  has a high absolute value because of the energy involved in the polaron formation and it does not show any noticeable temperature dependence as long as the phonons involved in the polaron formation are not frozen [25]. The anisotropy ratio  $S_{ab}/S_c \sim 6$  remains unchanged with lowering temperature.

The thermal conductivity ( $\kappa$ ) of WS<sub>2</sub> was measured employing a steady-state method. In general the total thermal conductivity includes a phonon and an electronic contribution ( $\kappa_e$ ). However, as expected from the low electrical conductivity of WS<sub>2</sub>, the electronic contribution to  $\kappa_e$  evaluated with the Wiedemann–Franz law is much less than 1 W/mK. We can therefore consider the phonons as the major mediators of heat current in WS<sub>2</sub> and one can neglect the electronic contribution in further discussions. The basal thermal conductivity ( $\kappa_{ab}$ ) is presented in Fig. 3(a). It increases from 124 W/mK at 300 K to 395 W/mK at 65 K where a broad maximum appears. The observed temperature dependence is typical of crystalline materials and it is due to Umklapp phonon scattering. However the absence of a  $\kappa_{ab} \propto T^3$  trend at low temperature and the relatively small increase of  $\kappa_{ab}$  with cooling indicate the presence of disorder in the bulk structure. The thermal conductivity component measured parallel to the  $c$ -axis ( $\kappa_c$ ) (Fig. 3(b)) displays a room-temperature value of 1.7 W/mK that is comparable to the



**Fig. 2.** Thermoelectric power as function of temperature measured parallel to the WS<sub>2</sub> planes (black curve) and perpendicular to them (red curve). Hole-like carriers prevail at high temperatures in both directions.

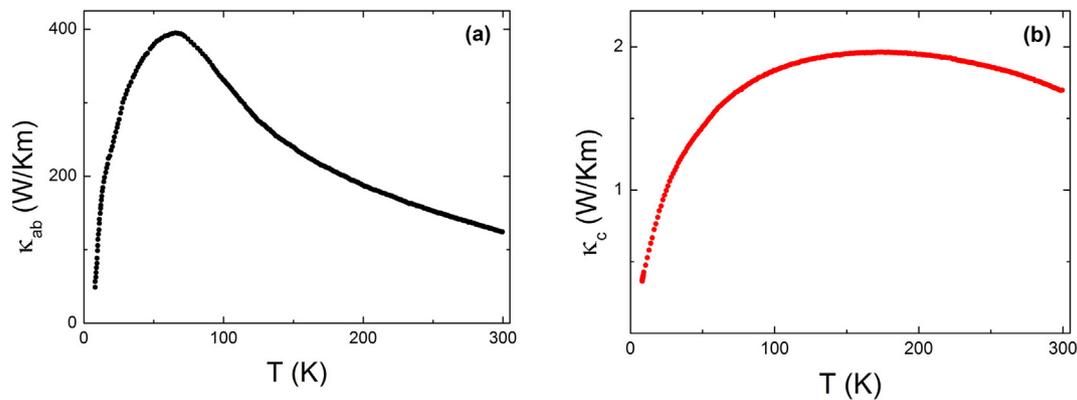


Fig. 3. (a) Temperature dependence of basal thermal conductivity of  $WS_2$ . (b) Out-of-plane thermal conductivity of  $WS_2$  single crystal.

theoretical estimate using the Slack equation [26] and is close to the value reported for  $WSe_2$  ( $\kappa_c = 1.5$  W/mK) [27]. The anisotropy  $\kappa_{ab}/\kappa_c \sim 70$  is higher than that observed in pyrolytic graphite [28], which can be explained by the different strengths of the in-plane and the out-of-plane bonds. The covalent nature of the bonds along the  $WS_2$  layer facilitates the propagation of phonons while heat conduction between different layers is very much reduced due to the weak Van der Waals bonds. The much shorter phonon mean free path could be qualitatively seen by the broad maximum at high temperatures (180–200 K). Below this temperature  $\kappa_c$  resembles that of disordered solids [29]. It is likely that the very same inter-plane disorder, which results in a much stronger activation in  $\rho_c$ , gives the glassy character to  $\kappa_c$ . An additional source of scattering of phonons could be at the interfaces between different layers, as has been shown for  $WSe_2$  [27].

In conclusion we have measured the anisotropic electrical resistivity, Seebeck coefficient and thermal conductivity of  $WS_2$  single crystals grown by chemical vapor transport employing sulfur as a transport agent. Resistivity shows thermally activated temperature dependence both parallel and perpendicular to the  $WS_2$  planes with an activation energy much lower than the bandgap, demonstrating that electronic transport is dominated by in-gap impurity levels. The high positive room temperature value of S confirms holes as the dominating type of charge carriers. Similarly to bulk  $MoS_2$ , the temperature dependence of S suggests a polaronic character of the charge carriers that is a strong electron phonon interaction. The thermal conductivity shows a very high anisotropy  $\kappa_{ab}/\kappa_c \sim 70$  rendering a two-dimensional nature thermal transport in  $WS_2$ . The in-plane  $\kappa(T)$  presents the characteristic features of crystalline materials while interlayer phonon scattering causes low values of  $\kappa_c(T)$  with a temperature dependence typical of amorphous materials. We believe that these features should be taken into consideration in designing single layer and hetero-structure devices with  $WS_2$ .

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