

# Tuning of electronic and vibrational properties of transition metal selenides $T\text{Se}_2$ ( $T = \text{Os}, \text{Ru}$ ) and their metallization under high pressure

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In recent decades, considerable interest has been focused on the structural, electronic, optical, and chemical properties of transition metal dichalcogenides (TMDs)  $\text{TX}_2$  (T is a transition metal cation and X is a chalcogen anion) [1–6]. The weak van der Waals bonding [1] between the two-dimensional TMDs atomic layers allows the formation of various low-dimensional structures that can compete with graphene in important technical applications, including nanoelectronics, photonics and energy storage [7, 8]. In this case, TMDs exhibit a significant variety of electronic properties [1].  $\text{OsSe}_2$  is a diamagnetic semi-metal with a pyrite-type structure [9, 10].  $\text{RuSe}_2$  is a diamagnetic semiconductor with an indirect band gap at ambient pressure [11, 12]. In recent studies of superconductivity in TMD with a pyrite-type structure, the relationship between superconductivity and structural instability, which involves the destabilization of anionic dimers, has often been discussed. In  $\text{PdSe}_2$ , such destabilization is caused by the application of external pressure [13], and in  $\text{IrSe}_2$  by Rh doping [14]. This kind of structural instability leads to a decrease in the frequency of the stretching  $A_g$  Se-Se mode due to an increase in the length of the Se-Se bond, as demonstrated by Raman spectroscopy.

However, for the  $\text{PdS}_2$  and  $\text{NiSe}_2$  dichalcogenides with a pyrite-type structure, it was shown that the destabilization of anionic dimers is not necessary for the occurrence of superconductivity, and such destabilization is not a sufficient condition for the formation of superconductivity [15]. Therefore, in  $\text{PdS}_2$  there is no correlation between the softening of the S-S dumbbell bonds and the dependence  $T_c(P)$ . Meanwhile, despite the elongation of Se-Se bonds under

pressure in  $\text{NiSe}_2$ , the sample remains a normal non-superconducting metal. Some correlations can also be expected between the pyrite-type structure of TMDs and the appearance of a superconducting state. In this direction, it is interesting to study and compare the transport properties and phonon modes of osmium diselenide  $\text{OsSe}_2$  and ruthenium diselenide  $\text{RuSe}_2$  under high-pressure conditions.

In our studies monocrystalline  $\text{OsSe}_2$  and  $\text{RuSe}_2$  samples were synthesized by the chemical vapor transport method. The stoichiometry of the obtained crystals was proved using energy dispersive X-ray spectroscopy. A screw-clamped diamond anvil cell equipped with 550- $\mu\text{m}$  culet diamond anvils was used for the simultaneous Raman spectroscopy and electrical resistivity measurements at high pressure up to 43 GPa.

Raman spectroscopy measurements were performed to study the evolution of the vibrational properties of  $\text{OsSe}_2$  and  $\text{RuSe}_2$  under high pressure. Weakening of Se-Se chemical bonds in  $\text{OsSe}_2$  and  $\text{RuSe}_2$  samples under high pressure was not observed, which is confirmed by a constant increase in the frequency of the  $A_g$  mode with pressure in both compounds.

Moreover, our Raman spectroscopy studies did not reveal any indication of structural phase transitions up to pressures of about 40 GPa. Thus, it can be assumed that the pyrite-type structure remains stable up to the highest pressures attained in the experiments.

We also performed electrical transport measurements to detect electronic transitions under applied pressure in  $\text{OsSe}_2$  and  $\text{RuSe}_2$  samples. It turned out that the resistivity of both samples at room temperature decreases with increasing applied pressure (Fig. 1). The similar effects reported in [13, 15] were associated with a substantial overlapping of the conduction and valence bands.

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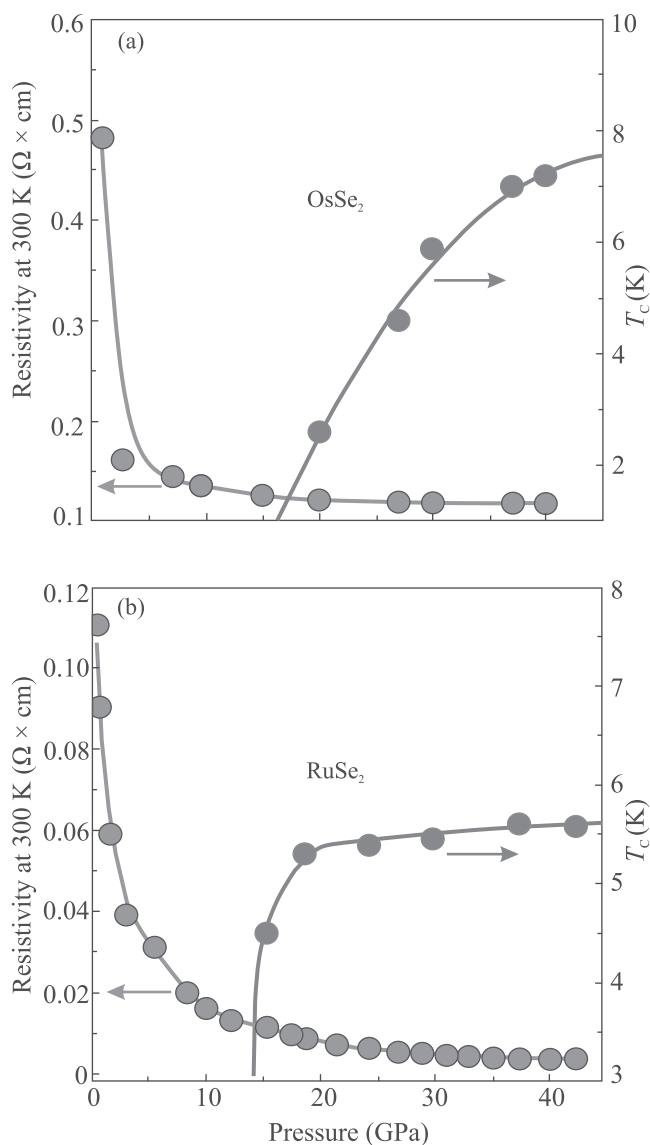


Fig. 1. (Color online) Room temperature resistivity and the onset temperature  $T_c$  of the superconducting transition for  $\text{OsSe}_2$  (a) and  $\text{RuSe}_2$  (b) compounds plotted as a function of pressure

At pressures in the range of 20–40 GPa, the electrical resistance of the sample  $\text{OsSe}_2$  drops in the temperature range of 2–6 K, which can be caused by the transition to the superconducting state. The  $\text{RuSe}_2$  sample also demonstrates a transition to the superconducting state under application of pressure. A noticeable drop in resistivity at low temperatures is observed at pressures above 15 GPa and extends up to 43 GPa (Fig. 1).

Thus, in contrast to  $\text{Ir}_{1-x}\text{Th}_x\text{Se}_2$  or  $\text{PdSe}_2$ , the appearance of superconductivity in  $\text{OsSe}_2$  and  $\text{RuSe}_2$  is not due to a phase transition or instability of anionic dimers. For both materials, a superconducting transition is observed at pressures above the transition to the metallic state, which is achieved during the slow evolu-

tion of semimetal into metal under pressure. An increase in the  $T_c$  critical temperature with pressure was found for both samples.  $\text{OsSe}_2$  demonstrated the classic dome-shape behavior of  $T_c(P)$  dependence, while for  $\text{RuSe}_2$ , the  $T_c$  remains constant above 35 GPa. For both materials, no indications of a structural phase transition were found in our spectroscopic studies up to the highest pressures.

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