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Thermoelectric properties of the intercalate crystals $Cu_x TiSe_2$ ($x = 0.025$, 0.58) at pressure up to 10 GPa

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Single crystals of two intercalated compounds, $Cu_x TiSe_2$ ($x = 0.025$, 0.58), were studied using the method of thermoelectric measurements under pressure. Experimental data for the pressure dependencies of thermoelectric power (Seebeck coefficient) and electrical resistance were obtained in the range of quasi-hydrostatic pressure up to 10 GPa. It is found that $Cu_{0.025} TiSe_2$ crystals are characterized by semiconductor conductivity, which conserve with pressure rising up to $1-3$ GPa. The bandgap value and pressure dependency of relative change of thermoelectric power factor were estimated in the semiconductor phase. For $Cu_{0.58} TiSe_2$ crystals, which displayed metallic conductivity, the bulk modulus of the high-pressure phase was determined. Furthermore, the impact of multiple cyclic compression on the electrophysical properties of $Cu_x TiSe_2$ crystals was thoroughly investigated.

Keywords high pressure, transition metals chalcogenides, phase transition, intercalates, thermoelectric power.

1. Introduction

In recent years, layered quasi-two-dimensional (2D) transition metal dichalcogenides (TMD) have been actively studied. Interest in these materials is due to their diverse physical properties and the possibility of wide application in various fields [1–3]. These materials have a layered structure, and weak van der Waals forces act in the space between the layers. The introduction of transition metal atoms into the van der Waals gap (intercalation) of TMDs results in a modification of their electronic structure and a change in transport properties [4]. Previously, using the example of $TiSe_2$ TMD, it was shown that the intercalation of copper atoms in low concentrations leads to the semimetal — semiconductor transition [5], and $Cu_x TiSe_2$ semiconductor crystals may have a number of interesting properties — electronic, thermoelectric, etc. The possibility of transition between different electronic states in TMDs through intercalation opens the way to the possibility of developing devices with different functional elements built on the basis of a single material.

With an intercalation with foreign atoms, one of the factors for modifying electronic properties is the expansion of the van der Waals gap. This effect can be partially compensated for by uniform compression of the crystals. This makes it possible to produce and study new electronic states under conditions of applied external pressure, and the presence of structural or electronic transitions under pressure significantly expands the range of potentially achievable electrophysical and optical properties in the compressed TMDs.

This study is focused on the thermoelectric properties of $Cu_{0.025} TiSe_2$ and $Cu_{0.58} TiSe_2$ intercalates under cyclic compression of crystals with a pressure of up to ~ 10 GPa. Baric dependences of thermoEMF and electrical resistance are obtained. For the $Cu_{0.025} TiSe_2$, in the region of existence of the semiconductor phase, estimates of the band gap and thermoelectric power factor are obtained. The bulk modulus of $Cu_{0.58} TiSe_2$ in the region of high-pressure phase is determined.

2. Experiment

Single crystals of $Cu_{0.025} TiSe_2$ and $Cu_{0.58} TiSe_2$ were grown using direct sublimation technique in evacuated quartz ampoules from the polycrystalline phase. The chemical composition of the synthesized samples was determined using electron fluorescence analysis technique on a JEOL-733 spectrometer, and after the measurements the X-ray microanalysis (EDAX spectrometer) was used on a QUANTA 200 Pegasus (FEI) and a Tescan MIRA LMS (Tescan Brno s.r.o.) scanning electron microscopes at the center of share equipment of the Institute of Metal Physics of the Ural Branch of the Russian Academy of Sciences. Chemical analysis of the $Cu_x TiSe_2$ samples after measurements under pressure showed that the compositions remained the same within the setup error. The crystal structure of the $Cu_x TiSe_2$ samples was studied using a Shimadzu XRD 7000 Maxima diffractometer (radiation source: $Cu K_\alpha$, graphite monochromator) at the Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences. The crystal structure was determined to be $P\bar{3}m1$. For more details on these methods, please refer to [6,7].

Measurements of thermoEMF under pressure were carried out on an original high pressure setup with carbide

anvils [8]. This setup makes it possible to study the thermo-electric and electrical properties of materials under uniform compression in the conditions of quasi-hydrostatic pressure. The anvils in this setup are made of VK6 hard alloy and have a hemispherical shape; the forces on the anvils are transferred by a mechanical press. Heaters are connected to the anvils to create a temperature gradient. The constant gradient is controlled using temperature sensors located in the upper and lower anvils. The ThermoEMF was measured using two electrical contacts [9]. The force applied to the anvils was determined using special strain gauges and converted into a pressure value via special calibration curve. The diameter of the working surface of the anvils was about 1 mm. The sample was placed in a toroidal limestone container, which served as both a dielectric spacer and a pressure transfer medium. Typical sample sizes were $\sim 150 \times 150 \times 50$ mkm^3. The measurements were carried out with repeated cyclic increases and decreases in pressure.

3. Experimental results and discussion

At a normal pressure, the coefficients of thermoEMF (S) of $Cu_{0.025}TiSe_2$ and $Cu_{0.58}TiSe_2$ were about -72 mkV/K and -10.3 mkV/K, respectively, indicating the predominance of *n*-type carriers.

A sharp decrease in the absolute value of thermoEMF in $Cu_{0.025}TiSe_2$ was discovered with increasing pressure to $1-3$ GPa (Figure 1, *a*) and in the electrical resistance (R) with increasing pressure to $1-2$ GPa (Figure 1, *b*), which was observed for all pressure cycles. This is indicative of the closing of the semiconductor gap and the transition of the $Cu_{0.025}TiSe_2$ sample to the metallic state. Previously, the possibility of formation of a semiconductor gap at insignificant degrees of copper intercalation was reported in [5]. Above 5 GPa, the baric dependence curves of thermoEMF change their slope, but retain a linear dependence on pressure (inset in Figure 1, *a*). Previously, it was reported about a change in the slope of the thermoEMF curves of TiSe$_2$ near the structural transition at $\sim 4-5$ GPa [5]. This transition was determined from X-ray diffraction data [10]. Probably, the change in the slope of the baric dependences of thermoEMF, as well as the hysteresis of the baric dependences of $Cu_{0.025}TiSe_2$ above 5 GPa, may be associated with a phase transition.

For non-degenerate or partially degenerate semiconductors, the dependence of thermoEMF (S) on the band gap E_g and the ratio of hole and electronic conductivity is determined from the following expression [11]:

$$S = - \frac{k}{|e|} \left[\frac{\sigma_n - \sigma_p}{\sigma_n + \sigma_p} \frac{E_g}{2kT} + \left(r_n + \frac{5}{2} \right) \frac{\sigma_n}{\sigma_n + \sigma_p} \right.$$
$$\left. - \left(r_p + \frac{5}{2} \right) \frac{\sigma_p}{\sigma_n + \sigma_p} - \frac{3}{4} \ln \frac{m_p^*}{m_n^*} \right], \qquad (1)$$

where k is Boltzmann constant, T is absolute temperature, e is electron charge, $\sigma_n(\sigma_p)$ is electron (hole) contribution
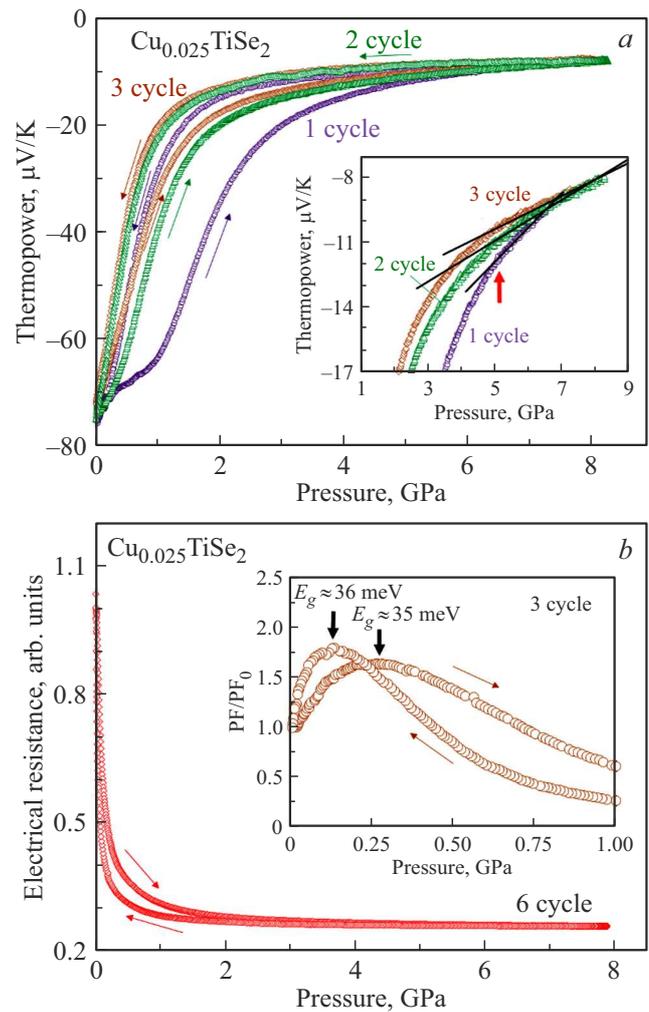

Figure 1. Baric dependences of thermoEMF (*a*) and relative change in electrical resistance (*b*) for different cycles of compression and decompression for $Cu_{0.025}TiSe_2$ crystals. The inset (*a*) shows in a different scale the same dependencies when compressed. Inset (*b*) shows the baric dependence of the relative change in the thermoelectric power factor for the third cycle of compression and decompression. Thin arrows show the direction of pressure change. The thick red arrow in the inset (*a*) points out a knick that may be associated with a structural transition.

to electrical conductivity, $r_n(r_p)$ and $m_n^*(m_p^*)$ are scattering parameters and effective masses of the density of states of electrons (holes), respectively. In the approximation that $\sigma_n \gg \sigma_p$, having obtained the dS/dP coefficient from the graph (Figure 2) and taking into account that $k/|e| \approx 86.4\mu$ V/K and $2kT \approx 50$ meV at $T = 300$ K, the baric band gap coefficient (dE_g/dP) was estimated for each compression and decompression cycle. By extrapolating the thermoEMF curves to „zero", the values of „metallization pressure" were approximately estimated for each cycle of increasing pressure. Taking into account the stability ranges and the calculated coefficients dE_g/dP, the values of E_g at normal pressure were estimated for each cycle of

compression followed by decompression. The values of E_g for $Cu_{0.025}TiSe_2$, determined for all cycles, were almost the same and amounted to $\sim 42-43$ meV (inset of Figure 2).

The dependence of the relative change in the thermoelectric power factor of $Cu_{0.025}TiSe_2$ (PF/PF_0, where $PF = S^2/R$ and $PF_0 = PF$ at 0 GPa) on pressure was assessed for the 3rd cycle of compression and decompression and it was found that the factor increases by 1.5 times at $P = 0.15-0.3$ GPa (inset in Figure 1, b). Using the above estimates of the band gap and its pressure coefficient, the value of $E_g \approx 35-36$ meV was determined, which corresponds to the maximum thermoelectric power factor. Previously, it was reported that under normal conditions the highest thermoelectric power factor is achieved in the $Cu_{0.02}TiSe_2$ and $Cu_{0.06}TiSe_2$ compounds [12]. At the same time, the maximum value of the thermoelectric figure of merit $ZT = 0.15$ ($ZT = PF \cdot T/\lambda$, where λ being thermal conductivity) was obtained for the $Cu_{0.11}TiSe_2$ compound at a temperature of 540 K [12]. According to [5], in the $Cu_{0.11}TiSe_2$ compound at room temperature the band gap should be about 36 meV. Apparently, optimal thermoelectric characteristics in Cu_xTiSe_2 intercalates are observed for compounds with the band gap reaching values of about $35-36$ meV. However, these values of E_g are noticeably smaller than the corresponding values of E_g in typical semiconductor thermoelectrics ($E_g \sim 150-250$ meV, which corresponds to the energy range of $6-10\,kT$ at 300 K) [13].

For $Cu_{0.58}TiSe_2$ an increase in the absolute value of thermoEMF was found with increasing pressure to $0.3-0.7$ GPa (Figure 3). Above this pressure, the absolute value of thermoEMF of $Cu_{0.58}TiSe_2$ gradually decreases. It is known that intercalation of metals in $TiSe_2$ results in hybridization of valence states of the intercalant and $Ti3d_{zz}$ orbital of titanium [14,15]. The bond energy of hybrid states depends on the ionization potential of the intercalated metal I_i in the observed charge state. If I_i is small, then the hybrid states are located above the Fermi level and are released with charge transfer to the conduction band of $TiSe_2$. If I_i exceeds a certain threshold, then the hybrid states are located below the Fermi level of $TiSe_2$. In this case, a covalent complex is formed, which acts as a trap for free electrons and as a center of lattice deformation of compression type along the normal to the basal plane [16,17]. The gain in energy of electrons during their localization is equal to the lattice deformation energy [18]. As shown in [19], at a copper content $x = 0.58$, the Fermi level is already in the region of localized states. However, to form a full-fledged complex, it lacks compression-type deformation along the normal to the basal plane. The anisotropy of compressibility along the basal plane and along the normal to it results in a situation that the main deformation is associated with the approach of the layers to each other in the $TiSe_2$. Consequently, at a pressure below $0.3-0.7$ GPa, the external pressure stabilizes covalent complexes. And at higher pressures, these complexes decompose and free electrons are released. This effect was observed, for example, in the Fe_xTiSe_2 system [20]. The irreversibility
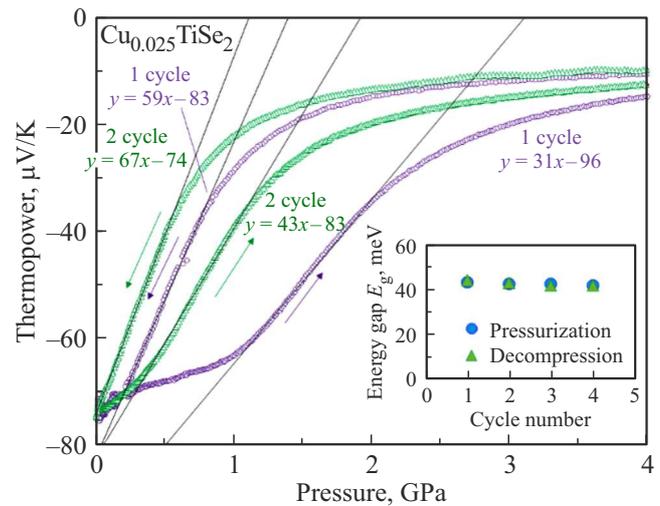

Figure 2. (a) Baric dependence of thermoEMF for the first and the second cycles of compression and decompression of $Cu_{0.025}TiSe_2$ crystals. In the semiconductor phase, thermoEMF curves can be described by linear functions, from which the baric thermoEMF coefficients can be estimated (dS/dP). The inset shows the dependence of the estimated energy gap using formula (1) with compression and decompression as a function of the cycle number.
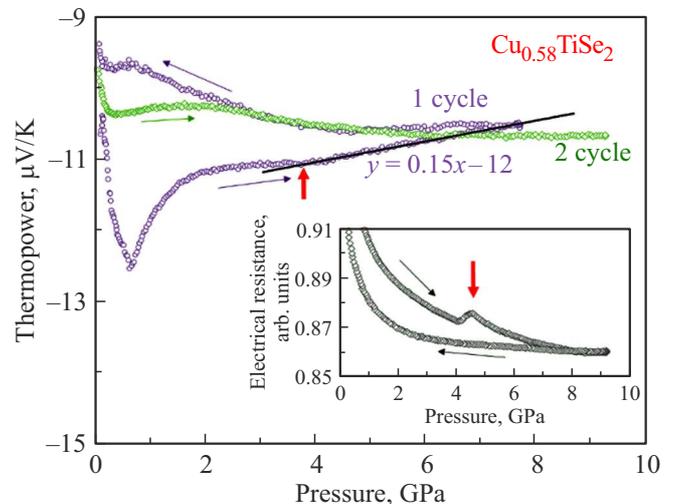

Figure 3. Baric dependence of thermoEMF for the first and the second cycles of compression and decompression of $Cu_{0.58}TiSe_2$ crystals. The inset shows the baric dependence of the electrical resistance. Thin arrows show the direction of pressure change. The thick red arrow points out a knick that may be associated with a structural transition.

observed in subsequent cycles may be due to the fact that the decomposition of complexes is a first-order transition with its inherent hysteresis. In $Cu_{0.025}TiSe_2$ the Fermi level is located significantly below the region of hybrid states [19], therefore such an effect was not observed for it (Figure 1).

At 4 GPa, a clear knick is visible in the thermoEMF dependence $Cu_{0.58}TiSe_2$, and a sharp jump is observed

in the electrical resistance dependence. Probably, this knick may also be associated with a structural phase transition [10].

In pure metals, diffusion thermoEMF (S_d) is determined by the formula [21]:

$$S_d^i = \frac{\pi^2 k^2 T}{3e\mu}\, x_i, \qquad (2)$$

where k is Boltzmann constant, T is absolute temperature, e is electron charge, μ is chemical potential (Fermi energy), $x_i = -(\partial \ln \rho / \partial \ln \varepsilon)_\mu$, where ρ is electrical resistance of a pure metal, and ε is electron energy. Pressure affects the atomic volume (V) and, therefore, the effect of volumetric compression on thermoEMF can be estimated from the following expression:

$$d(\ln S_d)/d \ln V = -d \ln \mu / d \ln V + d \ln x_i / d \ln V,$$

the second term describes changes in the electronic structure and phonon spectrum [21]. If the structure of the electronic bands is assumed remaining unchanged $d \ln x_i / d \ln V = 0$, and in the approximation of free electrons $-d \ln \mu / d \ln V = +2/3$, hence, with a reduction in volume (increase in pressure) the absolute value of thermoEMF should decrease. In metallic $Cu_{0.58}TiSe_2$ above $0.3-0.7$ the absolute value of thermoEMF decreases. Knowing the baric coefficient of thermoEMF, the bulk modulus (K) can be estimated. As can be seen from Figure 3, $dS/dP = 0.15\,\text{mkV}/(\text{K} \cdot \text{GPa})$ above $4\,\text{GPa}$, we get $K \approx 49\,\text{GPa}$. As reported in [10] $K \approx 33\,\text{GPa}$ for binary $TiSe_2$ in the high pressure phase. That is, according to the above estimates of the bulk modulus, the introduction of copper atoms into the $TiSe_2$ structure makes this material noticeably stiffer.

4. Conclusion

The study has investigated the behavior of the electronic properties (thermoEMF and electrical resistance) of titanium diselenide crystals ($Cu_x TiSe_2$) with varying degrees of intercalation by copper atoms ($x = 0.025$, 0.58) under conditions of uniform quasi-hydrostatic compression at gradual and cyclic increase (up to $10\,\text{GPa}$) and decrease in pressure. For the $Cu_{0.025}TiSe_2$ compound, the region of existence of the semiconductor phase under pressure is determined and the change in the band gap is estimated. Thus, at normal pressure, the semiconductor gap is estimated to be of the order of $42-43\,\text{meV}$ and gradually decreases with increasing pressure, and after repeated cyclic application of high pressure this value remains unchanged. It has been established that the optimal value of the thermoelectric power factor for this compound is achieved at a pressure of $P \sim 0.15-0.3\,\text{GPa}$.

The $Cu_{0.58}TiSe_2$ has metallic conductivity over the entire pressure range studied. During the studies, signs of an irreversible first-order phase transition were discovered

above a pressure of $0.7\,\text{GPa}$ associated with the appearance and subsequent decomposition of covalent complexes. For this crystal at pressures above $4-5\,\text{GPa}$, the bulk modulus was determined, the value of which turned out to be 1.5 times higher in comparison with non-intercalated titanium diselenide.

The results obtained expand the existing diversity of electronic properties of intercalated $TiSe_2$, including those under high pressure conditions.

Conflict of interest

The authors declare that they have no conflict of interest.

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