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LATTICE DYNAMICS  
AND PHASE TRANSITIONS

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## Phase Transitions in Titanium Diselenide Intercalated with Cobaltocene at High Pressures of up to 20 GPa

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**Abstract**—The pressure dependences of the kinetic properties of TiSe<sub>2</sub> intercalated with cobaltocene (bis-cyclopentadienyl-cobalt, CoCp<sub>2</sub>) and cobaltocene itself were measured. Anomalies are revealed in the pressure dependences of the resistance and thermopower (for the intercalated material), which are interpreted as pressure-induced structural phase transitions. The main effect of pressure on the molecules of cobaltocene as an individual compound and in the intercalated state is suppression of the intramolecular motion in the form of rotation of the cyclopentadienyl rings. The general character of the pressure effect on the kinetic properties of (CoCp<sub>2</sub>)<sub>x</sub>TiSe<sub>2</sub> agrees well with the assumption that the bonding of the organic molecules to the host lattice is covalent.

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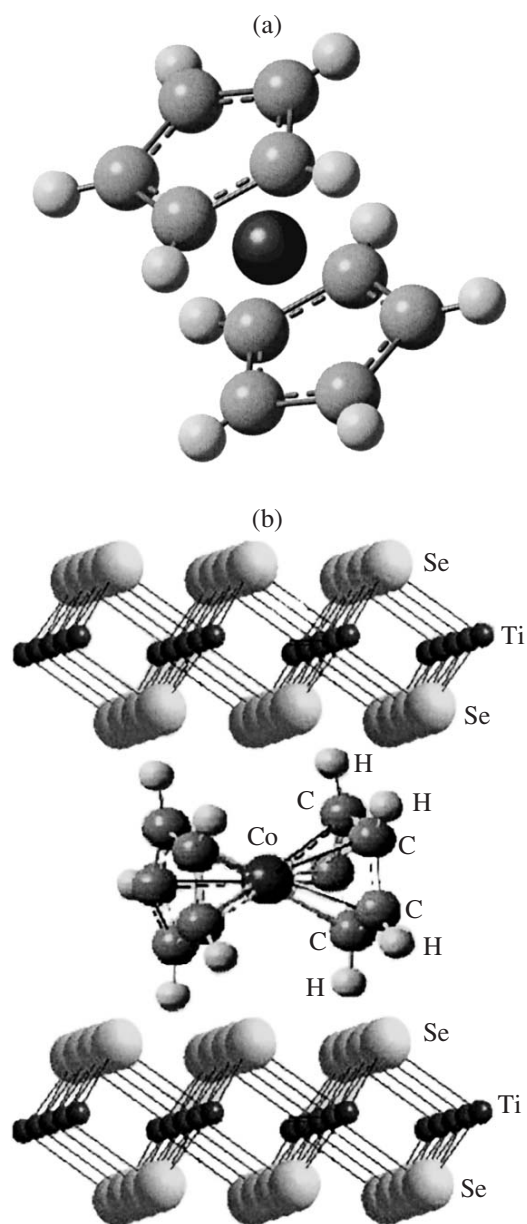
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The crystal structure of layered titanium dichalcogenides is a stack of building blocks consisting of a monatomic titanium network coordinated on both sides to monatomic chalcogen layers. All of the atomic networks are packed into a hexagonal closely packed motive. This construction is called “sandwich” in the literature. The weakness of the bonding between the sandwiches permits one to implant in the space between them various objects, including organic molecules [1]. This allows the formation of nanosized layered structures in which crystalline layers alternate with layers of organic molecules. At present, the character of the chemical bonding between organic layers and sandwiches is unclear. Analyzing the electrical and magnetic properties of the (MCp<sub>2</sub>)<sub>x</sub>TiSe<sub>2</sub> systems (*M* = Fe, Co) [2] revealed that this bonding is covalent. In this case, the regular arrangement of the layers of intercalated molecules and the host lattice with respect to each other is very important, because it provides overlap of the orbitals of molecules and lattice atoms that are responsible for the covalent bonding. The mutual arrangement of the layers can be changed by applying an external pressure, since one might expect that the compressibilities of the layers of organic molecules and the host lattice will differ strongly in magnitude. Studying the pressure dependences of the electrical properties (which are determined by the concentration and mobility of free charge carriers) can clarify the nature of the chemical bonding in this type of materials.

In this work, we studied the pressure dependences of the electronic kinetic properties of TiSe<sub>2</sub> single crystals intercalated with cobaltocene (CoCp<sub>2</sub>) in comparison with the properties of cobaltocene itself. The structure of cobaltocene consists of two parallel inverted pentagons with CH groups at the vertices and a cobalt atom at the midpoint between the pentagons. The orientation of the molecule in the lattice as determined from the increase in the interlayer spacing of the TiSe<sub>2</sub> lattice caused by an implanted cobaltocene [2] is shown schematically in Fig. 1.

Measurements were performed on single-crystal TiSe<sub>2</sub> samples intercalated with cobaltocene to the (CoCp<sub>2</sub>)<sub>0.25</sub>TiSe<sub>2</sub> composition. The technique of preparing the samples and their characterization is described in detail in [2].

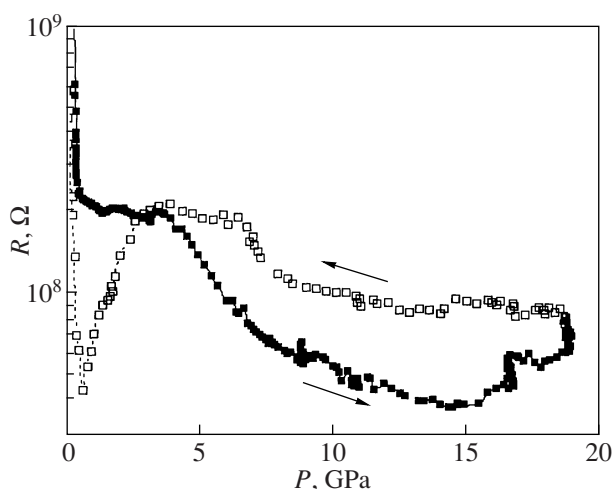
Measurements of the thermopower *S* and the electrical resistance *R* of microscopic samples with characteristic sizes of 0.2 × 0.2 × (0.01–0.05) mm were carried out using chambers made from conducting synthetic diamonds [3]. The pressure *P* in a layer of lithographic stone being compressed was determined from calibration curves (which were constructed using the phase transformation points of reference materials, such as ZnSe and CdTe) with an accuracy of better than ~10% [3]. The technique of measuring *S*(*P*) and *R*(*P*) is described in [4]. The measurements were performed on an automatic device permitting simultaneous recording of pressure, temperature difference, and the signal from



**Fig. 1.** (a) Structure of the cobaltocene molecule and (b) its position in the  $\text{TiSe}_2$  lattice (schematic).

the sample [5]. Simultaneously with measurement of the thermoelectrical properties, we recorded the sample compression  $\Delta x$  under pressure using electronic and mechanical dilatometers.

Figure 2 shows the pressure dependence of the resistance of the initial cobaltocene. Two anomalies related to a change in the resistance are clearly seen: (i) at a pressure  $P = 1$  GPa, the resistance decreases sharply approximately tenfold with subsequent relaxation to the initial value and, (ii) at pressures  $P > 15$  GPa, a slight increase occurs. The dip in the resistance observed at  $P = 1$  GPa with decreasing pressure can be related to a phase transition, while the nature of the

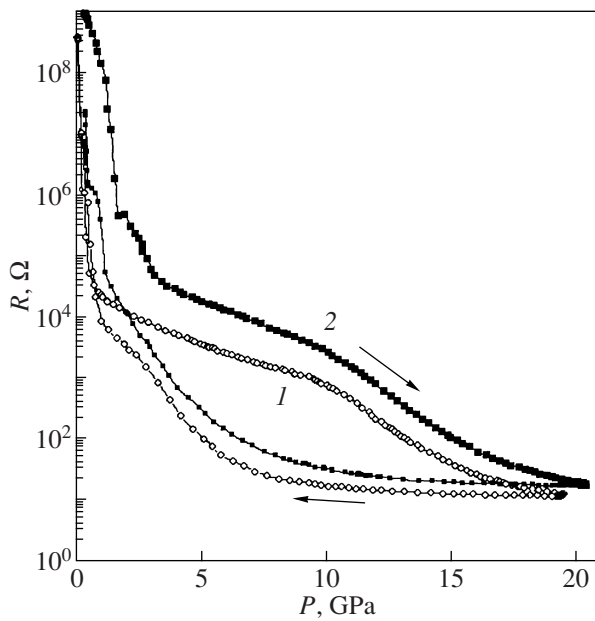


**Fig. 2.** Pressure dependence of the electrical resistance of  $\text{CoCp}_2$  at  $T = 293$  K measured with increasing and decreasing pressure.

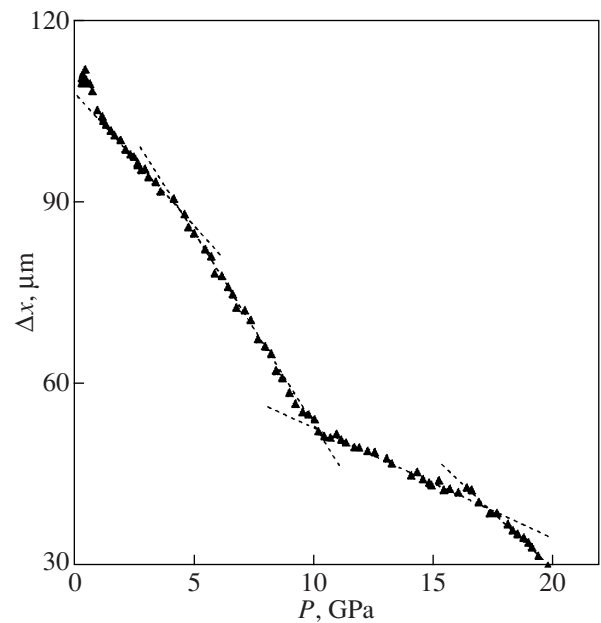
increase in the resistance at  $P > 15$  GPa is unclear. These anomalies were reproduced during two cycles of increasing and decreasing pressure. Naturally, the question arises as to the nature of the phase transition at  $P = 1$  GPa. The pressure can have a twofold effect on metallocenes. First, it can change the intramolecular structure; for example, it can “freeze” the rotation of cyclopentadienyl rings. Second, the external pressure can change the mutual orientation of molecules and lead to their closer packing and a change in the crystal structure.

It is likely that the anomaly at  $P = 1$  GPa is associated with an intramolecular reconstruction. This assumption is supported by the absence of any anomaly in the field dependence obtained with increasing pressure. Indeed, as the pressure increases, the freezing of rotation of the cyclopentadienyl rings fixes their random arrangement and has practically no influence on the degree of overlapping of the orbitals of individual molecules and, therefore, on the value of the resistance against the background of the general decrease in the resistance due to the decrease in the intermolecular distance. As the pressure decreases, the rings begin to rotate near  $P = 1$  GPa and an additional mechanism of charge transfer arises, which manifests itself as a sharp dip in the pressure dependence of the resistance. According to available thermodynamic data, the phase transition associated with freezing of rotation of the cyclopentadienyl rings is of second order [6].

For the  $\text{TiSe}_2$  samples intercalated with cobaltocene, the pressure dependences of the resistance exhibit two anomalies (Fig. 3): (i) at a pressure  $P \approx 1.5 \pm 0.5$  GPa, the resistance  $R$  decreases abruptly and, (ii) at pressures of  $\sim 10$  to 15 GPa, the pressure coefficient of  $R$  increases significantly. It is natural to relate these anomalies to phase transformations analogous to those occurring in the initial cobaltocene. Indeed, the anomaly near  $P =$



**Fig. 3.** Pressure dependence of the electrical resistance of  $(\text{CoCp}_2)_{0.25}\text{TiSe}_2$  for two subsequent cycles of increasing and decreasing pressure (the direction of the change in pressure is indicated by arrows).



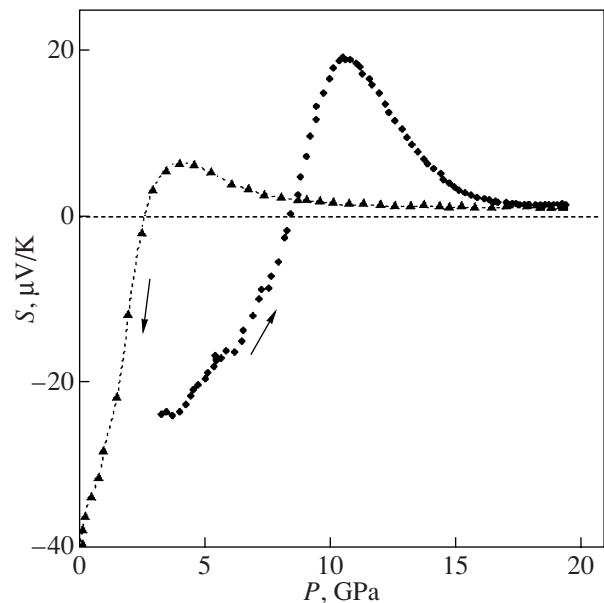
**Fig. 4.** Pressure dependence of the deformation of a  $(\text{CoCp}_2)_{0.25}\text{TiSe}_2$  sample (corresponding to cycle 2 in Fig. 3) after the subtraction of the linear contribution. The breaks in the curve correspond to a change in the compressibility and are related to phase transitions.

1.5 GPa is not accompanied by significant changes in the compressibility (Fig. 4), as in the case of freezing of rotation of the cyclopentadienyl rings. However, the pressure dependence of the deformation  $\Delta x$  of the sample (Fig. 4) shows anomalies at  $P \geq 10$  GPa, as might be expected if the position of cobaltocene molecules is changed with respect to the  $\text{TiSe}_2$  lattice. Thus, the anomaly in the electrical resistance observed in the range  $P = 5\text{--}15$  GPa can be related to a change in the packing of  $\text{CoCp}_2$  molecules due to compression of the intercalated layer.

The above specific features were reproduced during two cycles of increasing pressure. The low values of  $R$  and the pressure coefficient  $dR/dP$  observed at  $P$  higher than  $\sim 15$  GPa (Fig. 3) allow the assumption of the metallic conduction in this pressure range. The pressure dependence of the thermopower  $S$  shown in Fig. 5 confirms this assumption, since, over the range  $P > 15$  GPa, the values  $|S| \sim 1 \mu\text{V/K}$  are as low as those for typical metals and are slightly dependent on pressure. Since the initial cobaltocene remains an insulator over the entire pressure range, the charge transfer occurs through the  $\text{TiSe}_2$  lattice as it was observed in misfit compounds  $(\text{PbS})_n\text{TiSe}_2$ , wherein the building block  $\text{PbS}$  is only a reservoir of charge carriers and creates a scattering potential for conduction electrons, but it does not seem likely to be involved in the charge transfer [7].

In the range  $P \approx 1.5 \pm 0.5$  GPa, the anomaly of the resistance is accompanied by a relatively abrupt increase in the pressure coefficient of  $|S|$  (Fig. 5). Since

the nearest neighbors of the intercalated molecules are Se atoms, one might expect the formation of covalent bonds due to hybridization of the states of cobaltocene with the outer  $\text{Se}4p$  states. As is known, the charge carriers in  $\text{TiSe}_2$  at room temperature are both electrons in



**Fig. 5.** Pressure dependence of the thermopower of  $(\text{CoCp}_2)_{0.25}\text{TiSe}_2$  measured with increasing and decreasing pressure.

the Ti3d conduction band and holes in the Se4p valence band [8]. In this case, the Seebeck coefficient is close to zero far from the temperature of the transition to the charge-density-wave state, which indicates that the contributions from both types of charge carriers are practically equal [9]. The fact that the electronic contribution to the thermopower of  $(\text{CoCp}_2)_{0.25}\text{TiSe}_2$  is strongly dominant can be explained only in terms of the disappearance of the hole contribution, since, if only an increase in the electron concentration occurred, the Seebeck coefficient would decrease (as is the case, for example, for lithium donor doping [10]) rather than increase to  $\sim +20 \mu\text{V/K}$ . The capture of holes can be explained in terms of the formation of covalent bonds between  $\text{CoCp}_2$  and Se atoms. The breakage of these bonds leads to an increase in the hole concentration and gradual compensation of the electron contribution.

The phase transition occurring in the range 5–15 GPa is structural, as demonstrated by the change in the compressibility in this pressure range. This structural reconstruction can be associated only with reconstruction of the cobaltocene subsystem, since there are no phase transitions in  $\text{TiSe}_2$  in this pressure range [11]. According to calculations [12] performed for cobaltocene intercalated in  $\text{SnS}_2$  (material isostructural to  $\text{TiSe}_2$ ), the interaction of metallocene molecules with the host lattice leads to the presence of several stable positions differing in terms of the distance between molecules and their mutual orientation. In accordance with the calculations, the difference between the binding energies of molecules to the lattice in these stable positions is small (0.01–0.03 eV). At the same time, the work required to compress the  $\text{TiSe}_2$  lattice at a pressure of 10 GPa (at which the structural transition starts) is  $\sim 0.2 \text{ eV}$  [13] without considering the influence of the intercalated cobaltocene on the lattice compressibility. Clearly, the changes in the  $\text{TiSe}_2$  lattice size induced by such pressure can lead to a preferential orientation of the molecules with respect to the host lattice. The transition can not essentially change the charge carrier concentration and the shift in the Fermi level, since the reconstruction of the electronic structure related to the breakage of the  $\text{CoCp}_2$ – $\text{TiSe}_2$  covalent bonds is completed at lower external pressures. Thus, the effect of pressure on the conductivity and thermopower over this pressure range is associated with a change in the charge carrier mobility.

Thus, the effect of an external pressure on the electrical properties of both  $\text{CoCp}_2$  and  $\text{TiSe}_2$  intercalated by  $\text{CoCp}_2$  can be explained in terms of the same model that was used to explain the structural and magnetic properties of these compounds. According to this model, the intercalation with metallocene molecules results in the formation of covalent bonds between the

guest molecules and the host lattice. This effect is similar to that observed in the case of the intercalation with transition and noble metals, with the only difference that, in the case of metals, covalent bonds are due to hybridization of the valence state of an impurity with the Ti3d states, whereas in the case of metallocenes the Se4p states are hybridized.

## ACKNOWLEDGMENTS

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