Pressure-induced insulator–metal transition in a novel layer metalloorganic structure

Sergey V. Ovsyannikov, Vladimir V. Shehennikov, Alexander N. Titov, and Yoshiya Uwatoko

1 The Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba 277-8581, Japan
2 The Institute of Metal Physics of Russian Academy of Sciences, Ural Division, GSP-170, 18 S. Kovalevskaya Str., Yekaterinburg 620041, Russia

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A novel layer metalloorganic structure (Co(η^5-C_5H_5)_2)_0.25TiSe_2 has been synthesized by intercalation of the cobaltocene, Co(η^5-C_5H_5)_2 [bis(eta-5-cyclopentadienyl)cobalt] (a representative of the metallocenes M(η^5-C_5H_5)_2 where M – is a metal) into van-der-Waals gaps of TiSe_2 matrix. The papers reports a study of the electrical resistance \( R \), thermoelectric power \( S \) (Seebeck effect), and contraction of a sample’s thickness (compressibility) under almost continuous variation of quasihydrostatic pressure \( P \) within 0–20 GPa at room temperature. We observed a gradual decrease of \( R(P) \) by ~8 orders to 20 GPa. About \( P \sim 10 \) GPa we established both an abrupt change of \( dR/dP \) and inversion of \( S \) from the electronic to the holes type of conductivity. To \( P \sim 16 \) GPa the intercalate became a metal and exhibited a “close to zero” \( S \), which was kept down to 8 GPa on decompression; all pressure-induced changes were reversible. The synthesized compound (Co(η^5-C_5H_5)_2)_0.25TiSe_2 is a novel functional material for wide application.
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1 The Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba 277-8581, Japan
2 The Institute of Metal Physics of Russian Academy of Sciences, Ural Division, GSP-170, 18 S. Kovalevskaya Str., Yekaterinburg 620041, Russia

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1 Introduction

Cobaltocene, Co(η5-C5H5)2 [bis(eta-5-cyclopentadienyl)cobalt] is a typical representative of the metalloccenes – metalloorganic crystals based on pentadienyl C5H5 rings and containing one metal atom M(η5-C5H5)2. A unit cell of the metalloccenes consists of two parallel inverted pentagons with CH groups in tops and of metal atom in a centre between them (Fig. 1, left). Metalloccenes of all 3d-row elements are known, but with the exception of ferrocene, Fe(η5-C5H5)2 all of them are sensitive to air, paramagnetic and do not possess a closed-shell electron structure. Metalloccenes are widely used in technologies [1], for instance, ferrocene, [bis(eta-5-cyclopentadienyl)iron] is used as an additive for petroleum products [2]. Also a host of organic compounds for a wide range of applications are derivatives from the metalloccenes [3–6].

Titanium dichalcogenides TiX2 (X = S, Se, Te) possess a layer structure consisting of “sandwiches” (hexagonal close-packed Ti layer surrounded by two layers of chalcogens) separated by the van-der-Waals gaps (Fig. 1, right). A presence of the gaps opens opportunities for introduction (intercalation) of different objects into TiX2 [7] including alkaline, noble, transition and rare-earth metals, monochalcogenides of metals and organic molecules. Direct intercalation of transition metals (M) inside of TiX2 leads to a formation of covalent Ti–M–Ti centres, that results both in lowering of anisotropy and in reduction of magnetic moment of M. Whereas, preliminary “package” of metal atom inside of organic molecules
Fig. 1 (online colour at: www.pss-b.com) Crystal structure of cobaltocene, Co(η⁵-C₅H₅)₂ (left), and schematic view of the intercalation process: Co(η⁵-C₅H₅)₂ layers are introduced into van-der-Waals gaps of TiSe₂ matrix (right). The solid lines are chemical bonds. On the right figure the rhombuses point the location of octahedral voids, the closed symbols (Ti, Se) – atoms in the plane of the figure, whereas the open ones (Ti, Se) – atoms in the lower-laying plane.

prevents an overlapping of 3d-orbitals of Ti and M [8]. Intercalation of the metallocones leads both to extension of van-der-Waals gap by ~5.5 Å, and to charge transfer into matrix of layer compound [9]. During intercalation the pentagon planes are orientated perpendicular to TiSe₂ layers (Fig. 1, right) [9].

The goals of the present work were (i) to synthesize a novel metalloorganic structure by intercalation of cobaltocene into TiSe₂ matrix and (ii) to investigate a possibility of metallization and phase transitions in this structure in a pressure range of 0–20 GPa at room temperature by measurements of the electrical resistance, thermoelectric power, and contraction of sample’s thickness under pressure.

2 Experiment

Intercalation of cobaltocene (specification) into titanium diselenide matrix was performed in the tetrahydrofuran solution from the Co(η⁵-C₅H₅)₂ and TiSe₂ powders [10]. During intercalation purple colour of TiSe₂ changed into black. An equilibrium composition of the intercalate was established with an assistance of microprobe analysis at JEOL-733 microscope. (Co(η⁵-C₅H₅)₂)₀.₂₅TiSe₂ and polycrystals of Co(η⁵-C₅H₅)₂ were tested by the X-ray diffraction with CuKα radiation and Ni filter. It has been found that after intercalation a lattice constant of TiSe₂ matrix increased by 5.693 Å (from 6.008 Å to 11.701 Å).

The principal high-pressure investigator P. W. Bridgman pointed that simultaneous measurements of several properties under pressure are preferable as they give a fuller picture of substance’s behaviour [11]. So, the experiments were performed in the automated high-pressure setup permitting simultaneous registration of several parameters: electrical and thermoelectric signal from a sample, applied force (pressure), contraction of sample’s thickness, anvil’s temperatures, and thermal difference ΔT along a sample [12]. Ultra high quasi-hydrostatic pressure P was produced in synthetic diamond anvils possessing high electrical conductivity [12, 14–18]. A gasket from the lithographic stone (soft CaCO₃-based material) [18] served as a pressure-transmitting medium (Fig. 2). A sample of sizes ~0.25 × 0.25 × 0.05 mm³ was put into a hole ~0.25 mm in diameter drilled in the gasket [12, 14–18] (Fig. 2). Applied force was measured by a digital dynamometer with resistive-strain sensors. Values of pressure were estimated with ~10% uncertainty from the “stress-pressure” calibration curve based on the known pressure-induced transitions in Bi, ZnS, GaP and others [12, 14–18]. Synthetic diamond anvils were used both as electrical outputs to a sample and heater-cooler pair (upper anvil was heated) [12, 14–20]. S was
measured from \(\sim 3–4\) GPa, when \(R\) decreased to \(200–300\) k\(\Omega\). A contraction of a sample’s thickness was measured with an assistance of an electronic dilatometer conjunct with a mechanical one. In order to pick out a contribution of the sample itself from a full dependence of the anvils’ shift, we exclude the linear effects arising both from the elastic contraction of a chamber and contraction of the container.

3 Results and discussion

All \(R(P)\) dependencies obtained shown a gradual decrease of \(R\) by \(\sim 8\) orders to \(20\) GPa (Fig. 3a) attesting about transition from insulating into metal-like state. Also two peculiarities were noticed consisting in a change of slope, near \(P \sim 2–4\) (for different cycles) and \(9.5–10\) GPa (Fig. 3a). The curves of contraction of sample’s thickness also exhibited a change of slope near these pressure values (Fig. 3a) evidencing a variation of compressibility. The last circumstance permitted us to relate the above changes at \(R(P)\) to structural transformations. At \(P \sim 8–10\) GPa the thermopower of the sample inverted its sign to positive (Fig. 3b).

In the intermediate region from \(\sim 3–4\) up to \(9.5–10\) GPa a behaviour of the sample was similar to semiconductor, where the lowering of both electrical resistance (Fig. 3a) and thermopower (Fig. 3b) attested about narrowing of a semiconductor gap. Thermopower’s behaviour above \(P \sim 8–10\) GPa pointed out at a competition between electron and holes contributions into conductivity. Below \(P \sim 8–10\) GPa the electron contribution dominated, while above – the holes one (Fig. 3b). So, we attributed the first transition near \(2–4\) GPa to “insulator-semiconductor” type, and the second one at \(P \sim 9.5–10\) GPa to “electronic semiconductor – holes semimetal” type. Behaviour of \(R(P)\) and \(S(P)\) curves above \(P \sim 16\) GPa (as well as \(\Delta x(P)\)) evidenced a transition into metal state with “close to zero” thermopower. In some cycles we registered a back inversion of the thermopower’s sign above \(P \sim 17\) GPa (Fig. 3b, 1 cycle), while the absolute values were close to zero \(\sim 1\) \(\mu\)V/K. Small value of thermopower weakly depending on variation of pressure is known to be a typical feature of metals [20, 21]. Linear slopes of the dependencies of thermoelectric voltage on thermal difference \(\Delta T\) along a sample also corroborated such inversion of \(S\) (not shown on figures).

It is known that \(\text{TiX}_2\) crystals do not exhibit any significant variation in \(R\) and \(S\) in a range of \(0–20\) GPa at room temperature [22, 23], that is why we proposed the transitions discovered might be related to transformations in the guest \(\text{Co(}\eta^5\text{-C}_5\text{H}_5)\_2\) layers. We really found the similar variations of \(\text{d}R/\text{d}P\) for cobaltocene, \(\text{Co(}\eta^5\text{-C}_5\text{H}_5)\_2\) but at less pressures, near \(P \sim 1–2\) and \(3.5–7\) GPa, respectively (not shown on figures). Meanwhile, no metallization was observed in the cobaltocene itself under presurization up to \(22\) GPa at room-temperature.
Up to the present no high-pressure studies on metallocenes were reported, but in some others C₅H₅-based materials pressure-induced anomalies were noticed [24–27]. According to the theoretical calculations by the method of minimization of full free energy [28], the mutual orientation of cobaltocene molecules depends strongly on distance between them. The interaction between the molecules in metallocenes according to the calculations in Ref. [29] results in a possibility of existence of several stable states distinguishing both by distance between the molecules and by their mutual orientation. Contraction of a sample results in compression in distances between the molecules. So, the first transition observing by a bend of $R(P)$ near $P \sim 2$–4 GPa (Fig. 3a) might be due to such a change of mutual orientation of the molecules in the guest cobaltocene layer.

The second transition near $P \sim 9.5$–10 GPa (Fig. 3) might be related already to a structural transition inside of the molecule. It is known that application of high external pressure to cyclopentadienyl compounds is able to stop the dynamic reorientation of the cations [30]. For example, in order to stop a “molecular rotator” in ($\eta^5$-C₅H₅)($\eta^5$-C₅H₅)Fe(II)PF₆ one has to apply a pressure of $P \sim 1.79$ GPa [25]. While, “arrest” of rotation of pentadienyl rings was established to lead to a first order transition with a change of molecule structure from monoclinic to triclinic [30]. The transitions established need a direct structural detection.

The orientation transformations in Co($\eta^5$-C₅H₅)₂ layers might also result in a change of chemical bonds between the host and guest layers, and, hence, drastically vary a crystalline structure of the intercalate we observed by $R(P)$, $S(P)$, and $\Delta x(P)$ curves (Fig. 3). Because of disparity in compressibility of TiSe₂ and cobaltocene sub-lattices, the applied pressure leads to shift of molecules from their positions that could change the existing chemical bonds in the misfit also. It seems remarkably so great changes in properties of the soft metalloorganic intercalate, (Co($\eta^5$-C₅H₅)₂)₀.25TiSe₂, from insulating to metallic have fully-reversible character (checked for six sequent cycles).
4 Conclusion

A new functional layer metalloorganic crystal (Co(η⁵-C₅H₅)₂₀.₂₅TiSe₂) has been produced. The structure undergoes the reversible “insulator-semiconductor-metal” transition accompanying by ~8 order decrease in the electrical resistance, inversion of thermopower sign, and change of compressibility (Fig. 3). Neither cobaltocene nor TiSe₂ themselves exhibited any similar properties. To \( P \approx 16 \) GPa the intercalate completed a transition into metal. The transitions established near \( P \approx 2–4 \) and \( 9.5–10 \) GPa were related to structural transformations in the host layers of cobaltocene. We predict similar transitions are possible in other metallocones, M(η⁵-C₅H₅)₂(M – metal).

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