

Semiconductor-Metal Phase Transitions under High Pressure

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Abstract : We study the effects of high pressure on the electronic properties of the chain type TIMX₂ crystals. Calculations have been made for the variation of the energies of the main extremums of the conduction and valance bands. Decrease of the bandgap under pressure and semiconductor- metal phase transition in TlSe between 2.3 and 2.7 GPa under uniaxial pressure and ~5.14 Pa under hydrostatic pressure is found.

I. Introduction

Physicists over the past decades have extensively studied the low-dimensional materials that exhibit highly anisotropic properties. The ternary crystal TIMX₂ (M= Ga, In; X= Se, S, Te) belong to a family of low dimensional semiconductors possessing chain or layered structure. They are of significant interest because of their highly anisotropic properties, semiconductivity, photoconductivity, and potential applications for optoelectronic devices. They exhibit non-linear effects in their I-V characteristics (including a region of negative differential resistance), switching and memory effects. Electrical conductivity of several chain-type crystals exhibits time oscillations and intermittency. Second harmonic optical generation has been reported in TlInS₂. Layered TIMX₂ compounds were the first low-dimensional semiconductors in which a series of phase transitions with modulated structures was discovered. Furthermore, being doped with some impurity atoms or subjected to gamma-irradiation, TlInS₂ compound exhibits relaxor behavior and formation of the nano-sized polar domains. Thallium sulphide and thallium selenide nanorods, which show the quantum confinement effects, have recently been synthesized and studied.

Owing to the significant scientific interest, a lot of experimental techniques, such as x-ray and neutron diffraction, specific heat and dielectric measurements, nuclear magnetic resonance and electron paramagnetic resonance dielectric, sub-millimeter spectroscopy, IR spectroscopy, Raman and Mandelshtam-Brillouin scattering, inelastic neutron scattering, Mossbauer spectroscopy, etc. have been used to study these compounds. The great advantage in these studied is the opportunity of growing the sizable single crystals, which expanded the experimental potentialities of the investigators. Growing of mixed crystals (solid solutions) allows the design of materials with tailored properties for eventual applications in electronics and optoelectronics.

In contrast, TlSe, TlGaTe₂, TlInTe₂ and TlInSe₂ show chain structure [7,10], often called in literature as B37 TlSe type. The crystal structure of TlSe [7,10] belongs to the tetragonal symmetry, the space group is $D_{4h}^{18} - 14/mcm$, and the lattice parameters are $a = b = 8.02 \text{ \AA}$ and $c = 6.79 \text{ \AA}$, $z = 4$. TlSe is a mixed valence compound. Its formula should be more accurately written as $Tl^{1+}Tl^{3+}(Se^{2-})_2$. The trivalent and univalent thallium ions occupy two crystallographically inequivalent sites. The Tl^{3+} cations from covalent (sp^3) Tl-Se bonds and are located at the centers of $Tl^{3+}Se_4^{2-}$ tetrahedra, which are linked by common horizontal edges and form linear chains along the c -axis. The Tl^{3+} -Se distance, 2.67 \AA , is close to the sum of the covalent radii of Tl (1.49 \AA) and Se (1.17 \AA), respectively; the Se-Tl-Se angle is 115° . Each univalent Tl^{1+} cation is surrounded by eight chalcogen atoms, which form slightly deformed Thomson cubes, which are skewed by a small angle. Columns of Thomson cubes with common square faces are parallel to the c -axis and alternate with the columns of the aforementioned $Tl^{3+}Se_4^{2-}$ tetrahedra. Tl^{1+} -Se

distances are 3.43 Å, a little shorter than the sum of the ionic radii of Tl^{1+} (1.59 Å for CN=8) and Se^{2-} (1.98 Å). The Tl^{1+} and $Tl^{3+} - Tl^{3+}$ distances in the chains are 3.49 Å, while the distances between these atoms in the (001) plane are 5.67 Å. Each Tl^{1+} ion has four Tl^{3+} neighbors at 4.01 Å in the a, b -plane, and in reverse, each Tl^{3+} ion has four Tl^{1+} neighbors at the same distance. Projection of the TlSe structure on the (001) plane is shown in Figure - 1.

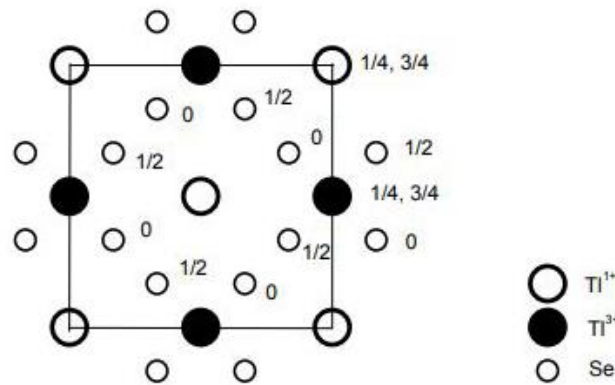


Figure-1 : Projection of the TlSe chain-type structure on the a, b -plane. The numbers 1/4, 1/2 and 3/4 are the z/c numbers.

II. Results and Discussion :

The effect of uniaxial pressure applied along and perpendicular to the tetragonal c axis, as well as isotropic hydrostatic pressure on the electronic band structure of TlSe, was first reported by Gashimzade and Orudzhev. The authors calculated the variation of the energies of the main extremums of the conduction and valence bands depending on the lattice constants a and c . The calculations predict decrease of the band gap under pressure and finally, semiconductor-metal phase transition in TlSe between 2.2 and 2.7 GPa under uniaxial pressure and ~ 5 GPa under isotropic hydrostatic pressure. Then Valyukonis et. al. and Allakhverdiev et. al measured the pressure dependence of the direct and indirect energy gaps E_g^d and E_g^i in TlSe, $TlInSe_2$, $TlInS_2$ and $TlInSe_{2(1-x)}S_{2x}$ ($0 \leq x \leq 0.25$) by analyzing the shifts of the fundamental absorption edges under applied pressure up to 5.5 GPa. (Here indices d and i denote direct and indirect gaps, respectively).

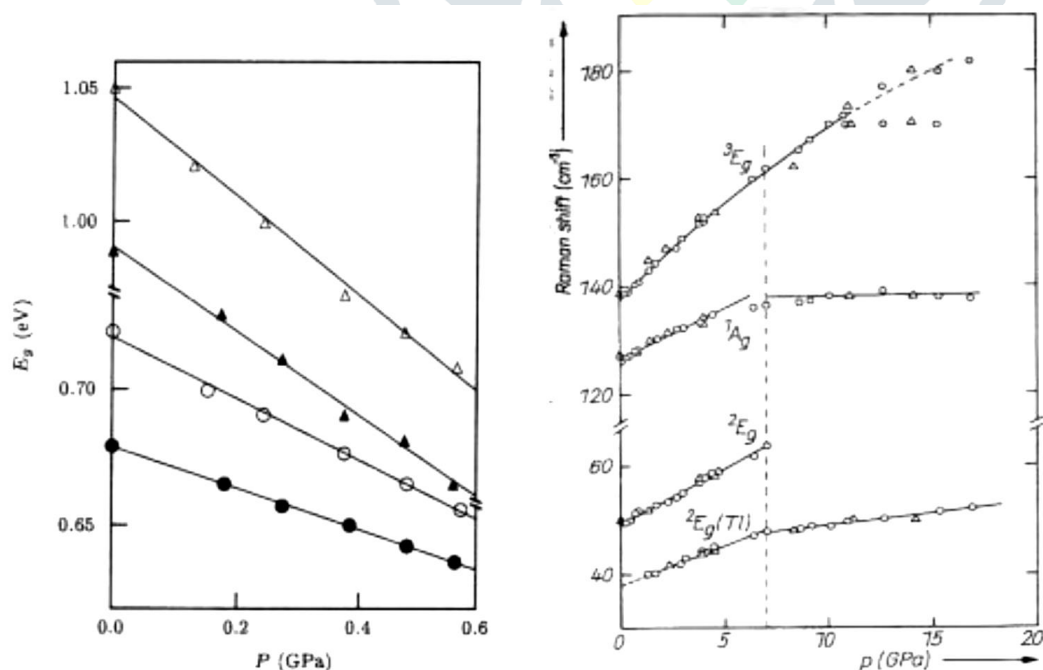


Fig. 2 - Left panel : Pressure dependence of the direct (triangles) and indirect (circles) band gaps in TlSe at room temperature measured for $\hat{E}||c$ (open symbols) and for $\hat{E} \perp c$ (bold symbols). Right panel : Raman shifts of phonon peaks in $TlInTe_2$ at room temperature as a function of pressure. The vertical dashed line delineates the pressure-induced phase transformation at about 7 GPa.

The absorption coefficient was calculated from the transmission spectra using the value of the refractive index. Both direct and indirect gaps were found to linearly decrease with increasing pressure (Figure-2) left panel), i.e., showing negative pressure coefficients dE_g/dP . These coefficients for TlSe were determined as $dE_g^d/dP = -0.15$ eV/GPa for $\hat{E} \perp c$, $dE_g^d/dP = -0.17$ eV/GPa for $\hat{E} \parallel c$, $dE_g^i/dP = -0.09$ eV/GPa for $\hat{E} \perp c$, $dE_g^i/dP = -0.11$ eV/GPa for $\hat{E} \parallel c$, respectively. (Here \hat{E} is the electric field vector of the electromagnetic wave). These data are in satisfactory agreement with the calculated ones. Some differences in dE_g/dP measured by different authors (e.g. $dE_g^d/dP = -0.125$ eV/GPa, and $dE_g^i/dP = -0.02$ eV/GPa in TlSe) may be caused by different quality of the investigated crystals. The pressure dependences of the band gap in the TlInSe₂ crystal were determined as $dE_g^d/dP = -0.11$ eV/GPa, and $dE_g^i/dP = -0.15$ eV/GPa. Since TlInSe₂ and TlInS₂ form a continuous series of mixed crystals in the whole range of concentrations ($0 \leq x \leq 1$), it was interesting to study the properties of these crystals. In the mixed crystals TlInSe_{2(1-x)}S_{2x}, dE_g^i/dP was shown to slightly decrease with increasing x , from -0.145 to -0.13 eV/GPa for $x = 0.05$ to 0.25 respectively. No phase transitions were observed up to pressures ~ 0.8 GPa in all aforementioned crystals. However, a structural phase transition, accompanied by a reversal of the sign of dE_g^i/dP , was reported in TlInSe_{0.2}S_{1.8} under pressure. Valyukonis et al ascribed the aforementioned pressure dependence of the band gap to the changes in the interchain interactions with pressure, which, in turn, may influence the positions of energy minima and maxima at the bottom of the conduction band and on the top of the valence band. Next, an abrupt change of dE_g^i/dP at $x \sim 0.3$ indicates a structural transformation, most probably from the tetragonal TlInSe₂-like crystal to the monoclinic TlInS₂-like crystal. Furthermore, TlInSe_{1.4}S_{0.6} shows a linear reduction of the band gap with increased pressure up to ~ 0.72 GPa; at this pressure the band gap changes abruptly. The authors assigned this change to the structural transformation under pressure. It was found that increasing amount of Se in the TlInSe₂-TlInS₂ system shifts pressure-induced phase transition to higher pressure. We note that Allakhverdiev et al. measured also the temperature dependence of the direct and indirect energy gaps.

Ves has measured the Raman spectra of the chain thallium indium telluride (TlInTe₂) crystal up to high pressure of 17 GPa at room temperature, using a diamond anvil cell. Three Raman peaks were observed in the low-pressure tetragonal phase. The pressure coefficients and the corresponding mode Grueneisen parameters γ of their frequencies were obtained. The modes were tentatively assigned by comparison to Raman spectra of related TlSe-type compounds. The frequency dependence of γ indicated that a hierarchy of bonding forces is present. The appearance and disappearance of a new Raman peak at about 1.75 GPa was presumably attributed to a gradual, pressure induced mutual replacement of In atoms by Tl atoms but not to indication of the occurrence of a structural phase transition. However, noticeable change in the slope of the pressure dependence of the Raman shift near 7.0 GPa was definitely assigned to a phase transition; furthermore, at even higher pressures indications for a second phase transition were found. We notice that, to our knowledge, the aforementioned explanation of the pressure evolution to the Raman modes, based on a pressure induced mutual interchange of In and Tl atoms, was never supported by the x-ray measurements.

Investigation of the crystal structures of thallium sulfide and thallium selenide under very high pressure, up to 37 GPa, has been carried out by Demishev et. al. using XRD technique and diamond anvil cell. Three first-order phase transitions were found in TlS: TlS I (TlSe-type) \rightarrow TlS II (α -NaFeO₂-type) \rightarrow TlS III (distorted α -NaFe₂O-type) \rightarrow TlS III (distorted α -NaFe₂O-type) \rightarrow TlS IV (CsCl-type) at 5, 10 and 25 GPa, respectively. The transition sequence is reversible. The space group of the first phase is D_{4h}^{18} -

14/mcm, and the lattice parameters were determined as $a = 7.77 \text{ \AA}$, $c = 6.79 \text{ \AA}$. For the second phase, the space group is $D_{3d}^5 - R3m$, and the lattice parameters are $a = 3.945 \text{ \AA}$, $c = 21.788 \text{ \AA}$, $Z = 6$. This phase II of TIS is metastable under normal conditions and reveals semiconductor properties. At that, the phase II \leftrightarrow phase III transition exhibits a hysteresis : the pressure of the direct transition II \rightarrow III is 10 GPa, while that of III \rightarrow II transition is 5.5 GPa. Phase IV of TIS appears near $P = 25 \text{ GPa}$, being mixed with the phase I and III in the pressure range from 25 to 30 GPa. At $P = 35.5 \text{ GPa}$, its x-ray pattern corresponds to the pure phase IV structure of CsCl type with $a = 3.202 \text{ \AA}$.

The compression of thallium selenide up to $P = 21 \text{ GPa}$ results in the first-order structural transition from the tetragonal TlSe I phase to the cubic TlSe II phase. The latter is of the CsCl-type. The transformation is realized by the shift of the selenium atoms from the position with $x = 0.25$, $y = 0.75$, $z = 0$. The authors suggest destroying of the covalent chains under phase transitions. The pressure-induced transition from TlSe I into TlSe II phase is accompanied by the reduction of the a/c ratio from 1.16 to 1 and reduction of the relative volume of the unit cell V/V_0 on 40%. TlSe II phase shows $a = c \sim 3.78 \text{ \AA}$. the Se - TI^{3+} and Se - TI^+ distances shortens as well, and hence the bond character is changed. Note that Se - TI distance of 2.9 \AA is longer than the sum of the covalent radii of TI (1.49 \AA) and Se (1.17 \AA), 2.66 \AA , but much shorter than the sum of the ionic radii of TI^{1+} (1.59 \AA for CN = 8 in the CsCl lattice) and Se^{2+} (1.98 \AA), i.e. 3.57 \AA , and is close to the sum of the ionic radii of TI^{3+} (0.98 \AA for CN=8) and Se^{2+} , i.e. 2.96 \AA , respectively. Such a bond is intermediate between the ionic and covalent ones.

Since TI^+ and TI^{3+} ions in the phase I and II of TIS and phase I of TlSe occupy different crystallographic positions, the charge transfer between them is structurally forbidden, and these phase are suggested to show semiconductor properties. One might assume metallic properties for the TIS IV and TlSe II phases since in the CsCl-type lattice TI^+ and TI^{3+} ions are structurally equivalent, and free charge transfer between TI^+ and TI^{3+} is structurally allowed. This hypothesis has to be verified by the electric conductivity measurements of TIS and TlSe under high pressure. We note that Demishev et. al. also determined the equations of state for TIS and TlSe.

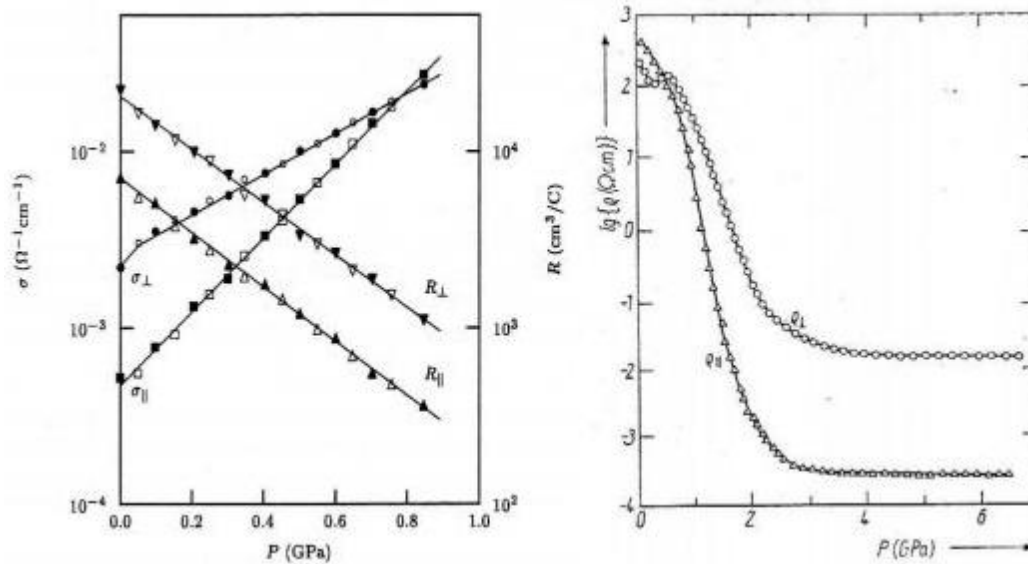
Pressure dependence of the electrical conductivity (as a rule, at room temperature) was reported by several authors. Kerimova et. al. obtained a gradual increase in the conductivity along the c axis in the undoped TlInSe_2 crystal, from $1.4 \times 10^{-6} \text{ Ohm}^{-1} \text{ cm}^{-1}$ at ambient pressure to $7.5 \times 10^{-5} \text{ \Omega}^{-1} \text{ cm}^{-1}$ at $P = 1.4 \text{ GPa}$. The authors realized that pressure behavior of the conductivity may be well fit by the equation.

$$\ln \sigma(P) = \ln \sigma(0) + AP \quad \dots\dots\dots(1)$$

where $A = d \ln \sigma(P)/dP = 0.34 \times 10^{-2} \text{ \Omega}^{-1} \text{ cm}^{-1} \text{ GPa}^{-1}$. Assuming exponential variation of the electrical conductivity with pressure

$$\sigma(P) = \sigma(0) \exp (-GP/2kT) \quad \dots\dots\dots (2)$$

where $G = dE_g^i/dP$, k is the Boltzmann constant and T is the temperature, the authors found that $G = 2kTA$. To satisfy the parameters G should be negative, since $A > 0$, and thus the band gap should decrease with increasing pressure, in accordance with that observed in the experiment.



In the figures, the left panel shows the pressure dependence of the parallel and perpendicular components of the electrical conductivity of TLSe. The right panel shows pressure dependence of the electrical resistivities of TLSe parallel and perpendicular to the c axis at ambient temperature.

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