Electrical Transport Properties and Band Structure of CuInSe₂ under High Pressure

Meiyan Ye,† Ruilian Tang,§ Shuailing Ma,§ Qiang Tao,‡ Xin Wang,‡ Yan Li,*‡§ and Pinwen Zhu*†§

†State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun 130012, China
‡School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, China
§Center for High Pressure Science and Technology Advanced Research (HPSTAR), Changchun 130012, China

ABSTRACT: Chalcopyrite-structured semiconductor CuInSe₂ has received considerable attention owing to its promising electrical and optical properties for nonlinear optical instruments and photovoltaic solar cells. In view of these interesting properties of CuInSe₂, it is thought to be worthwhile to study the high-pressure electrical transport behavior of this compound. Herein, we use in situ Hall-effect measurements, temperature-dependent electrical resistivity measurements, and first-principles calculations to conduct a comprehensive study on the carrier behavior and the band structure of CuInSe₂ under high pressure. The resistivity shows an obvious increase with pressure and reaches the maximum value at 7.2 GPa, indicating that pressure enlarges the band gap which has been confirmed by the result of the subsequent band structure calculations. Dramatic changes in electrical transport parameters, such as Hall coefficient, Hall mobility, carrier concentration, and electrical resistivity, are detected at 7.2 GPa, which are attributed to the structural phase transition from the chalcopyrite to the NaCl-type structure. In addition, a semiconductor-to-semiconductor transition is also observed to be associated with the structure transformation, which is different from the previous theoretical prediction. The result of the band structure calculations illustrates that CuInSe₂ reaches the maximum band gap of 1.201 eV at 7.0 GPa. However, the pressure coefficient of the band gap \( \frac{dE_G}{dP} \) is lower than that of similar binary compounds which can be explained by the combination of structural distortion effect and a p–d hybridization effect under pressure. These results provide a certain guiding role for the practical applications of the materials.

1. INTRODUCTION

Among the I–III–VІІ compounds, CuInSe₂ is widely used due to its superior electrical properties and important applications in photovoltaic devices. CuInSe₂ is a promising solar cell photovoltaic application material, which is inseparable from its excellent properties: high light absorption coefficient \( (10^{-5} \text{~cm}^{-1}) \); forming a structurally stable heterojunction with CdS to achieve high conversion efficiency; suitable band gap; low-cost production; low toxicity; intrinsic self-doping to adjust band gap and semiconductor conductivity types; no photo-induced attenuation effect; and good resistance to high-frequency radiation. In recent years, in order to develop a variety of methods for synthesizing CuInSe₂ and to better understand the electrical properties and optical properties under ambient pressure, a large number of theoretical and experimental studies have been carried out. These findings have important guiding significance for further development of the potential physical and chemical properties of CuInSe₂.

Over the past two decades, pressure as an alternative to external stimuli of temperature has been proven to be an effective tool for changing the structural and physical properties of functional materials. Under high pressure, CuInSe₂ changes its structure and enhances its light absorption coefficient and band gap, which indirectly affects its photovoltaic applications. González et al. performed an optical absorption edge measurement on the CuInSe₂ single crystal in the range of 10.0 GPa and observed that the pressure coefficient of band gap \( \frac{dE_G}{dP} \) linearly increased at a rate of 30.0 meV/GPa. According to the change in the light transmission characteristics of the sample under pressure, an irreversible structure phase transformation at 7.1 GPa was observed in CuInSe₂. By using high-energy dispersive X-ray diffraction measurement, this structural phase transition that occurred at 7.6 GPa has been identified as a tetragonal phase to a cubic phase with a 10% volume collapse. On further compression, another structural phase transition was detected at 39.0 GPa, and the high-pressure phase has been considered as the orthorhombic phase with space group \( Cmcm \). The I–III–VІІ compound semiconductor has a relatively narrow energy gap, and the pressure-induced changes of energy gap and electronic valence state have also attracted wide research.
interest. In addition, the electrical transport properties of CuInSe\textsubscript{2} can be viewed as important technical parameters that can influence its actual application, and the high-pressure electrical transport experiments have shown to be a powerful tool to investigate the electronic structure of semiconductors.\textsuperscript{22,23} However, the pressure effects on the electrical transport parameters of CuInSe\textsubscript{2}, such as electrical resistivity, Hall coefficient, carrier concentration, and carrier mobility, are still unclear. Can pressure be used as a one-dimensional effective means to further improve the electrical properties of materials? Based on the above questions, we thoroughly study the electrical transport properties of CuInSe\textsubscript{2} under high pressure and provide an important experimental basis for people to understand I–III–VI\textsubscript{2} compound semiconductors.

In addition, whether or not the semiconductor CuInSe\textsubscript{2} undergoes metallization transformation under high pressure is another significant subject. A previous theoretical study has showed that CuAlX\textsubscript{2} (X = S, Se, Te), which are analogues to CuInSe\textsubscript{2}, will change the structure from the tetragonal phase to the cubic phase under high pressure, and a pressure-induced metallization transformation was found accompanied by the transition.\textsuperscript{24} Pluengphon et al. predicted that the band gap of CuInSe\textsubscript{2} will be close to 15.0 GPa by \textit{ab initio} calculations, which means that the semiconductor-to-metal transition occurs at the critical pressure.\textsuperscript{25} In fact, we still need more direct and effective measurements to prove the metallization of CuInSe\textsubscript{2} under certain pressures.

In this paper, we report \textit{in situ} Hall-effect measurements performed on CuInSe\textsubscript{2} as a function of pressure. The pressure effect on the electrical transport behavior has been determined. At the same time, the mechanism for the variations of electrical transport properties under high pressure has been discussed, and these results can provide some experimental support for further research. Meanwhile, we also investigate the temperature dependence of electrical resistivity to verify the presence of metallization under pressure. In addition, we also try to use the first-principles calculation method to observe the changes in energy band structure and density of states under high pressure.

2. EXPERIMENTAL AND COMPUTATIONAL DETAILS

The CuInSe\textsubscript{2} was prepared by a hydrothermal method. Amounts of 1.26 mmol of CuCl\textsubscript{2}·2H\textsubscript{2}O, 1.29 mmol of InCl\textsubscript{3}·4H\textsubscript{2}O, and 2.59 mmol of Se powder were dissolved in 30 mL of anhydrous ethylenediamine and stirred for 30 min and then poured into a 50 mL Teflon-lined stainless steel autoclave.\textsuperscript{26} Successively, the autoclave was sealed and maintained at 180 °C for 24 h. After naturally cooling to room temperature, the precipitate was centrifuged three times with benzene, absolute ethanol, and distilled water, respectively, and finally dried at 80 °C for 4 h in a vacuum. The sample was characterized by X-ray diffraction at ambient conditions (Japan Rigaku D/max-\Gamma\textsubscript{a}X-ray diffractometer, equipped with graphite-monochromatized Cu K\textsubscript{\alpha}1 radiation (\(\lambda = 1.5406(4)\) Å), as shown in Figure 1(a).

The peak position and diffraction intensity match well with the tetragonal phase CuInSe\textsubscript{2} (JCPDS No. 87-2265). We performed Rietveld refinement to obtain the lattice parameters of CuInSe\textsubscript{2} under normal pressure: \(a = b = 5.797(1)\) Å, \(c = 11.601(4)\) Å, \(V_0 = 97.463(67)\) Å\textsuperscript{3}.

The chalcopyrite ternary compounds have an intrinsic self-doping effect, which can be controlled by the atomic molar ratio to accept different conductivity types. Therefore, we

![Figure 1](https://example.com/image1.png)

\(X = S, Se, M = \text{Metal (Cu+In)}, \rho = \text{resistivity}\)

**Figure 1.** (a) XRD survey spectra of the sample. (b) XPS survey spectra of the sample. (c) Conductive type dependent on the value of X/M, X = S, Se, M = Cu + In. (d) Configuration of a microcircuit on a diamond anvil.
measured the sample by X-ray photoelectron spectroscopy (XPS), as shown in Figure 1(b). The sample consists of Cu, In, and Se, and except for carbon as a reference and oxygen adsorbed on the surface, no other impurities were found. Further analysis shows that Cu, In, and Se elements each account for 22.45%, 23.73%, and 53.81%. According to the relationship shown in Figure 1(c), we suspect that the prepared sample should be a p-type semiconductor.27

High-pressure experiments were carried out using a nonmagnetic diamond anvil cell (DAC) with an anvil culet of 400 μm in diameter. A nonmagnetic rhenium flake was chosen as the gasket, and a hole of 150 μm in diameter was drilled as the sample chamber. The mixture of cubic boron nitride and epoxy was pressed onto the surface of the gasket for insulation. Fabrication of the detecting microcircuit on a diamond anvil, as shown in Figure 1(d), has been reported previously.28–30 A few ruby grains were loaded with the sample for pressure determination.31 No pressure-transmitting medium was used in order to avoid the introduction of impurities for interfering with the electrical measurement and ensure good electrical contact in the high-pressure in situ Hall-effect measurements. During the Hall-effect measurements, the magnetic flux density was measured by a Lakeshore 420 Guass meter. The electrical current was supplied by a Keithley 2400 current source, and the voltage was measured by a Keithley 2700 multimeter. The measurement process was automatically performed according to the van der Pauw method. The magnetic flux density applied to the sample was 1.2 T.

The first-principles calculations were based on density functional and pseudopotential methods, using the CASTEP software package in Material Studio.32 We used the Norm-conserving potential to describe the electron–ion interaction. The PBE (Perdew–Burke–Ernzerhof) form of the generalized gradient approximation (GGA) was used to describe the exchange-correlation function of the system.33 The grid was 5 × 5 × 6, and the cutoff wave can select 600 eV. The unit cell geometry optimization used in this paper was a complete structural optimization of atomic position and lattice constant at the same time, using the BFGS minimization algorithm.34 The space group of CuInSe2 was I4-2dd with the calculated lattice parameters a = b = 5.782 Å and c = 11.620 Å.35

3. RESULTS AND DISCUSSION

3.1. In Situ Hall-Effect Measurements under High Pressure. The electrical resistivity (ρ) of CuInSe2 as a function of pressure at room temperature is shown in Figure 2(a). The highest pressure reached 23.1 GPa in the experiment. Under ambient condition, the value of ρ is 1.33(2) Ω cm. As the pressure increases, the ρ increases slowly and reaches the maximum value of 6.10(2) Ω cm at 7.2 GPa. A dramatic inflection point in the variation trend of ρ is observed at this critical pressure. With further increasing pressure, the ρ decreases rapidly and drops over 2 orders of magnitude in the range of 7.2–23.1 GPa.

As shown in Figure 2(b)–(d), at ambient condition, the values of Hall coefficient (RH), carrier concentration (p), and carrier mobility (μ) are 9.93(3) cm3 C−1, 6.28(2) × 1017 cm−3, and 8.41(1) cm2 V−1 s−1, respectively. Because the positive RH was obtained at ambient pressure, the tetragonal phase CuInSe2 was considered as a p-type semiconductor, which is consistent with the results presumed by the XPS experiments. As the pressure increases, RH first increases from ambient pressure to 7.2 GPa and then begins to decrease. No pressure-driven p–n conduction type switching can be observed in the whole pressure region, unlike the situations that occurred in CuInS2 and CuFeS2.36,37 It can be seen from Figure 2(c) that the p decreases slowly with increasing pressure before 7.2 GPa and then turns to increase rapidly until 23.1 GPa. For μ, it shows almost identical variation trend with p in the whole pressure region. It is well-known that the resistivity can be expressed as

\[
\rho = \frac{1}{peμ}
\]

(1)

where ρ is the resistivity; p is the carrier concentration; e is the elementary charge; and μ is the Hall mobility. Thus, the increase of the ρ before 7.2 GPa is mainly caused by the quick decrease of μ, and the increase of p and μ together contributes to the decrease of ρ above 7.2 GPa. Quite obviously, both RH, p, and μ display an abnormal turning point at 7.2 GPa. Previous XRD and optical absorption experiments have proved that CuInSe2 experienced a structural phase transition around 7.0 GPa.19,20 Thus, the pressure-induced structure transformation of CuInSe2 can bring about a noticeable change in

![Figure 2.](image-url)
electrical transport properties. The phase transition point is less affected by nonhydrostaticity, unlike the situation that occurred in MnWO₄ and the structural stability of the sample is very sensitive to nonhydrostaticity conditions.³⁸

3.2. Temperature and Pressure Dependence of Resistivity. In order to check whether or not CuInSe₂ undergoes a pressure-induced semiconductor–metal transition along with the structural phase transition, we measured the temperature-dependent resistivity of CuInSe₂ at different pressures. As shown in Figure 3, the resistivity of CuInSe₂ is always kept decreasing with increasing temperature over the entire pressure range, indicating that both tetragonal phase and cubic phase perform a semiconductor behavior. This result is similar to the experimental result of CuFeS₂ and CuInS₂ but inconsistent with the theoretical calculation revealing that CuInSe₂ undergoes a metallization phase transition at 15.0 GPa.₂⁵,₃⁶,₃⁷ In addition, it also can be clearly seen from Figure 3 that when the pressure is less than 7.0 GPa the slope of the line used to linearly fit the temperature-varying resistivity increases slowly with the pressure, but when the pressure is greater than 8.6 GPa, the slope turns to decrease with the increase in pressure. In order to obtain the internal conduction mechanism of the carrier, we deduced the activation energy from the variable-temperature resistivity by eq 2

\[
\rho = \rho_0 \exp \left( \frac{E_a}{kT} \right)
\]

(2)

where \( \rho \) is the resistivity; \( \rho_0 \) is a prefactor; \( K \) is Boltzmann constant; \( E_a \) is the activation energy; and \( T \) is the temperature. On the basis of eq 2, we have

\[
E_a = K \left( \frac{\partial \ln \rho}{\partial T} \right)
\]

(3)

As can be clearly seen from Figure 4, the \( E_a \) increases with pressure at a rate of 16.27 meV/GPa below 7.0 GPa, indicating that the acceptor level increases with increasing pressure, resulting in a reduction in carrier capable of participating in conduction over the barrier, and ultimately leading to an increase in \( \rho \). On the contrary, the activation energy decreases rapidly with increasing pressure above 7.0 GPa, indicating that the pressure causes an increased overlap of the electron orbital wave function and narrows the energy gap. Therefore, the carrier transport becomes easier, and the \( \rho \) increases with increasing pressure, eventually resulting in a decrease in \( \rho \). The above results of the variation of the carrier concentration induced by the activation energy as a function of pressure are consistent with the previous Hall-effect results. The inflection point (7.2 GPa) of the activation energy of the carrier also indicates that the structural phase transition occurred herein.

3.3. Band Structure Calculations. In order to gain further insight into the change in the band gap of the tetragonal phase CuInSe₂, we have performed the first-principles calculations, as shown in Figure 5(a). The valence band maximum (VBM) and the conduction band minimum (CBM) of CuInSe₂ are located at the \( \Gamma \) point of the Brillouin zone and are characterized as a semiconductor conductivity with a direct band gap of 0.967 eV which is slightly smaller than previous study results (1.05 eV).⁴ The partial density of states (PDOS) at ambient pressure (Figure 5c) shows that the energy band in the range of \(-13.7 \, \text{eV} \) to \(-11.6 \, \text{eV} \) is mainly composed of the Se 4s state, and the band between VBM and \(-6.8 \, \text{eV} \) is composed by the hybridization of the Cu 3d state and the Se 4p state. Above the Fermi surface, the conduction band of CuInSe₂ is mainly composed by the Cu 3p state, In 4p state, and Se 4p state. As the pressure increases, all the energy bands are broadened, and the band gap reaches a maximum value of 1.201 eV at 7.0 GPa, as shown in Figure 5(b). Usually DFT underestimates the band gap but gives the correct pressure dependence.⁵⁰ The band gap increases with pressure at a rate of 33.4 meV/GPa which matches well with the pressure coefficient of the band gap \( dE_g/dP \) (30.0 meV/GPa) obtained by González et al.¹⁹ However, the \( dE_g/dP \) is lower than that of similar binary compounds.⁵⁰ The main reason is that, in addition to the structural distortion effect, the increases in hybridization of the Cu 3d state and Se 4p state, which can cause a reduction in band gap with pressure, are also considered.¹⁹,⁴⁰,⁴¹ It is well-known that the optical-absorption spectrum is a powerful tool to study the band gap behavior of materials.⁴² Therefore, the pressure-induced band gap behavior (opening from 0.967 eV at 0 GPa to 1.201 eV at 7.0 GPa) of CuInSe₂ will be tested by future optical-absorption experiments in the near-infrared region.

It is well-known that the main technical parameters that can influence the application of solar cells are: short circuit current

Figure 3. Temperature-induced resistivity changes at representative pressures.

Figure 4. Variation of activation energy of CuInSe₂ under pressure.
(I_0), open-circuit voltage (V_{oc}), fill factor (FF), and photovoltaic conversion rate. An increase of V_{oc} will result in an increase of FF and photovoltaic conversion rate, which means that the performance of the solar cell is superior. V_{oc} can be expressed as

\[ V_{oc} \approx \frac{n k T}{q} \ln \left( \frac{I_{ph}}{I_0} \right) \]  

where \( n \) is the diode curve factor; \( K \) is Boltzmann constant; \( T \) is temperature; \( q \) is electron charge; \( I_{ph} \) is photocurrent; and \( I_0 \) is reverse saturation current which is related to band gap. The pressure-induced band gap enlargement, obtained by our calculations results and previous experimental results, will reduce the \( I_0 \) and ultimately results in a corresponding increase in the \( V_{oc} \) which means that increasing the pressure in the tetragonal phase CuInSe_2 can optimize its performance for the application in solar cells.\(^{19}\)

4. CONCLUSIONS

In this study, we have performed the in situ Hall-effect measurements, the temperature-dependent resistivity, and the first-principles calculations, respectively. The Hall-effect results showed that the structural phase transition of CuInSe_2 that occurred at 7.2 GPa can cause significant changes in the electrical transport parameters. The resistivity decreases with increasing temperature below 21.0 GPa, indicating that the structural phase transition that occurred around 7.0 GPa is a semiconductor-to-semiconductor type transition. The activation energy of CuInSe_2 has been obtained and discussed. In addition, the calculations of the band structure and the density of states showed that the band gap increased with increasing pressure before the phase transition and reached a maximum value of 1.201 eV at 7.0 GPa.

■ AUTHOR INFORMATION

Corresponding Authors
*R. T.) E-mail: tangruilian626@cust.edu.cn. Phone: +86-431-85583188.
*R. L.) E-mail: liyan2012@jlu.edu.cn. Phone: +86-431-85168881.
*(P. Z.) E-mail: zhupw@jlu.edu.cn. Phone: +86-431-85168881.

ORCID
Yan Li: 0000-0002-1401-7925
Pinwen Zhu: 0000-0002-6357-5552

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Grant No. 11704142), by the Jilin Province Science and Technology Development Program, China (20170520119JH), and by the Open Project of State Key Laboratory of Superhard Materials (Jilin University).

