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A study on the electrical property of HgSe under high pressure*

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Using a microcircuit fabricated on a diamond anvil cell, we have measured in-situ conductivity of HgSe under high pressures, and investigated the temperature dependence of conductivity under several different pressures. The result shows that HgSe has a pressure-induced transition sequence from a semimetal to a semiconductor to a metal, similar to that in HgTe. Several discontinuous changes in conductivity are observed at around 1.5, 17, 29 and 49GPa, corresponding to the phase transitions from zinc-blende to cinnabar to rocksalt to orthorhombic to an unknown structure, respectively. In comparison with HgTe, it is speculated that the unknown structure may be a distorted CsCl structure. For the cinnabar-HgSe, the energy gap as a function of pressure is obtained according to the temperature dependence of conductivity. The plot of the temperature dependence of conductivity indicates that the unknown structure of HgSe has an electrical property of a conductor.

Keywords: in-situ conductivity measurement, phase transition, high pressure
PACC: 7280E, 8140R, 0735, 0750

1. Introduction

In II–VI compound semiconductors, the mercury-based compounds HgSe and HgTe represent an exceptional class because of their inverted band structure. The measurement of the Seebeck coefficient and resistivity behaviour of HgSe was carried out up to 2.5GPa and 523K, and confirmed the existence of an inverted band ordering.[1] HgSe has a zinc-blende (ZB, phase I) structure at atmospheric pressure and room temperature. The ZB HgSe transforms to a new phase (phase II, red HgS hexagonal structure) at a pressure near 0.75GPa and room temperature based on their electrical resistance measurements.[2] Above 0.75GPa, the resistance increases rapidly by six orders of magnitude and reaches a maximum at about 1.2GPa.[2]

The electrical properties of the cinnabar HgSe were investigated under hydrostatic conditions.[3] The resistance–temperature data suggested that the high-resistance phase is a semiconductor with a wide band gap, whose pressure coefficient is negative. The stronger interaction between the helical chains under compression has an effect of reducing the energy gap, i.e. $E_g = 0.43$ eV at 1.15GPa and $E_g = 0.35$ eV at 2.1GPa.[1]

Although mercury compounds attract less attention than the other zinc and cadmium compounds, the relationship between the resistivity and the pressure found in HgTe and HgSe suggests that they are very interesting materials.[4] They undergo transitions from a semimetal to a semiconductor to a metal, implying that the band structure changes and shifts as a function of pressure in an interesting way. The phase transition sequence of mercury chalcogenides is different from that usually found in ZB materials, in which the insulating fourfold-coordinated phase transforms to a sixfold-coordinated metal under high pressures.

In this paper, in-situ conductivity measurement of HgSe is carried out under high pressures. Our main purpose is to investigate the possible changes in conductivity, especially, at pressures above 20GPa, and to obtain the information on the energy gap and the phase transitions under high pressures.

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2. Experiment

We used a Mao–Bell type diamond anvil cell (DAC) and T301 stainless steel as the gasket. Pressure was determined by the ruby fluorescence method. The sample HgSe with a purity of 99.999%, purchased from Alfa Aesar Company, was ground into fine powder with an average size of 5μm.

Using a film deposition technique, a layer of Mo film with a thickness of 2μm was deposited on a diamond anvil surface as a conductor, topped with a layer of alumina film with a thickness of 3μm as the insulation film. A microcircuit was fabricated with a photolithographic shaping method after film encapsulation. The method of fabricating a microcircuit has been described in the previous works.[5−8] The microcircuit structure was slightly modified from quasi four-probe method to van der Pauw four-probe method.

The van der Pauw method with the following formula was utilized to calculate the conductivity of the sample

$$\exp(-\pi l R_{\rm A}\sigma) + \exp(-\pi l R_{\rm B}\sigma) = 1\,, \qquad (1)$$

where σ and l are the conductivity and the thickness of the sample, respectively; $R_{\rm A}$ and $R_{\rm B}$ are electrical resistances with $R_{\rm A} = V_{43}/I_{12}$ and $R_{\rm B} = V_{14}/I_{23}$. In the measurement, the current I_{12} was applied across the contacts 1 and 2, and the potential difference V_{43} across the contacts 3 and 4 was measured with a multimeter (Hewlett-Packard, 3458A); and similarly, the current I_{23} was applied across the contacts 2 and 3, and the potential difference V_{14} across the contacts 1 and 4 was measured.

3. Results and discussions

3.1. The conductivity of HgSe as a function of pressure at room temperature

The in-situ conductivity measurement was carried out under high pressure and room temperature. The result is shown in Fig.1.

As can be seen, the conductivity changes very little with increasing pressure from ambient pressure to about 1GPa. From 1 to 2GPa, however, the conductivity decreases abruptly by a factor of 10^4, corresponding to the phase transition from the ZB to the cinnabar. In our experiment, the pressure range of the phase transition is wider than the previous results[2,9] due to the fact that our pressure is not completely hydrostatic. In addition, the wider pressure scope of the phase transition is attributed to the sluggish nature of the lower-pressure transition from the ZB to the cinnabar.

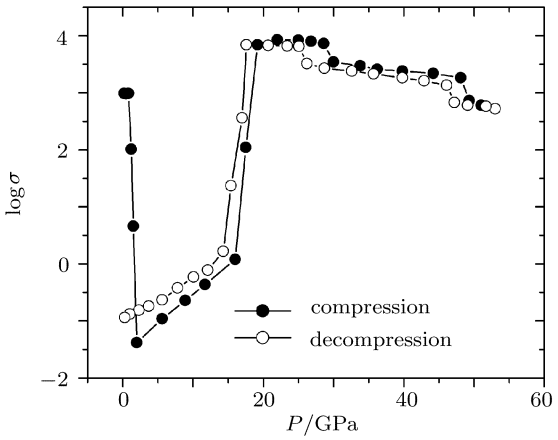


Fig.1. The conductivity of HgSe as a function of pressures at room temperature. σ is in unit of $\Omega^{-1}\cdot{\rm cm}^{-1}$.

From Fig.1, it can be observed that the conductivity rises gradually with increasing pressure from 2 to 16GPa. Within 16 to 18GPa, the conductivity increases abruptly by at least four orders of magnitude, corresponding to the phase transition from the cinnabar to the rocksalt structure. The conductivity reaches a maximum on the order of $10^4\Omega^{-1}\cdot{\rm cm}^{-1}$. Above 18GPa, the conductivity almost levels up to 28GPa. From 28 to 30GPa, the conductivity decreases discontinuously by about half an order of magnitude, corresponding to the transition from the rocksalt to the orthorhombic structure.

Upon further increasing pressure, another abrupt change in conductivity can be found at around 49GPa. We speculated that HgSe may undergo another phase transition from the orthorhombic to an unknown structure at this pressure. In comparison with HgTe, it is expected that the unknown structure may be a distorted CsCl structure.

Upon decompression, similar conductivity behaviour can be observed with a certain amount of hysteresis. However, the conductivity does not return to the original semimetal state until the pressure decreases to ambient pressure, indicating that the transition from the ZB to the cinnabar structure is not reversible.

3.2. The energy gap measurement of the cinnabar HgSe

We have measured the temperature dependence of conductivities of the cinnabar HgSe under several

pressures, as shown in Fig.2.

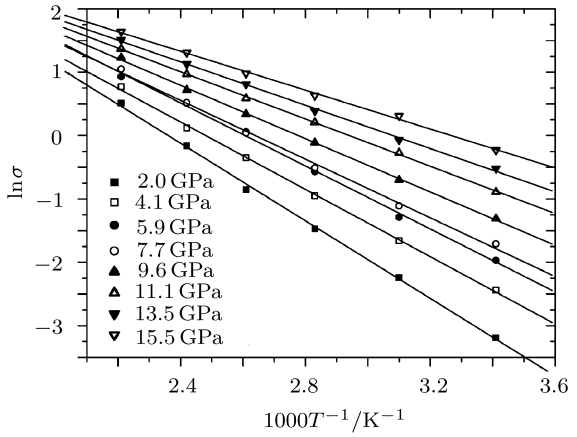


Fig.2. The plots of $\ln\sigma$ versus $1000/T$ of the cinnabar HgSe. σ is in unit of $\Omega^{-1}\cdot\mathrm{cm}^{-1}$.

In the intrinsic region, the relationship among the conductivity, the energy gap and the temperature of a semiconductor can be represented by the following expression:[10−12]

$$\sigma = \sigma_0 \exp(-E_\mathrm{g}/2k_\mathrm{B}T)\,, \tag{2}$$

where σ is the conductivity, E_g the energy gap, T the temperature in degrees Kelvin, k_B the Boltzmann constant, and σ_0 is a constant depending partially upon the electron and hole effective masses.

From Eq.(2), the relationship between the energy gap and the slope of $\ln\sigma$ versus $1000/T$ can be represented by the following equation:

$$E_\mathrm{g} = -2000k_\mathrm{B}\Big[\frac{\partial \ln\sigma}{\partial(1000/T)}\Big]. \tag{3}$$

The energy gaps are obtained by fitting linearly the plots of $\ln\sigma$ versus $1000/T$, as shown in Fig.3. Meanwhile, in order to show the relationship between E_g and $\ln\sigma$, the plot of $\ln\sigma$ versus p is also shown in Fig.3.

The plot of E_g versus p in Fig.3 is fitted to a quadratic function[13,14]

$$E_\mathrm{g} = E_{\mathrm{g}0} + \alpha p + \beta p^2\,, \tag{4}$$

where α and β are the first and second order pressure derivatives, respectively, $E_{\mathrm{g}0}$ is a constant. According to our experimental data, α, β and $E_{\mathrm{g}0}$ are calculated to be -0.27×10^{-2} eV/GPa, 4.6×10^{-4} eV/GPa^2 and 0.57 eV, respectively.

The decrease of the energy gap with increasing pressure is explained by the fundamental property of semiconductors, which is attributed to the band widening by strengthened overlap interaction of the wavefunction with shrinking of the atomic distance.[15]

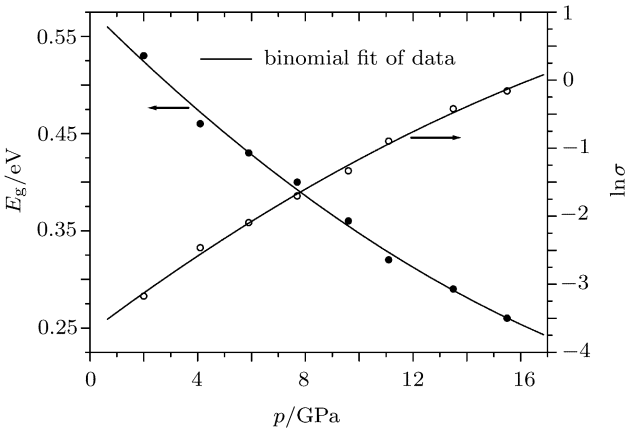


Fig.3. The plots of E_g versus p and $\ln\sigma$ versus p of the cinnabar HgSe at room temperature. σ is in unit of $\Omega^{-1}\cdot\mathrm{cm}^{-1}$.

3.3. The measurement of the temperature dependence of conductivity

We have measured the temperature dependence of conductivity of HgSe at several pressures, as shown in Fig.4.

As can be seen from Fig.4, the ZB HgSe exhibits the electrical property of a semimetal, characterized by $\mathrm{d}\sigma/\mathrm{d}T > 0$ and a large conductivity. For the cinnabar HgSe, $\mathrm{d}\sigma/\mathrm{d}T > 0$, which exhibits the electrical property of a semiconductor. For the rocksalt, orthorhombic and unknown structure HgSe, $\mathrm{d}\sigma/\mathrm{d}T < 0$, which exhibit the electrical property of a metal.

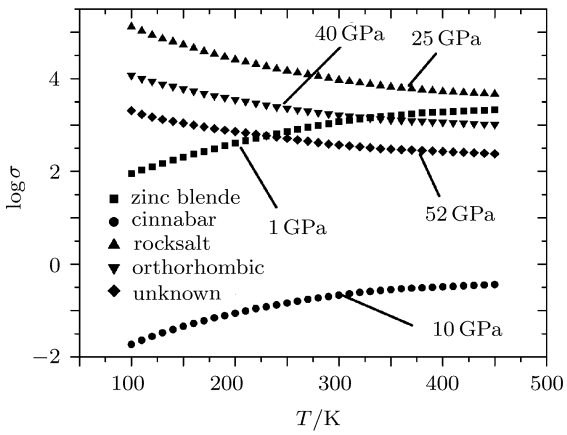


Fig.4. The temperature dependence of conductivity of HgSe at several pressures. σ is in unit of $\Omega^{-1}\cdot\mathrm{cm}^{-1}$.

4. Conclusions

Using a microcircuit fabricated on a DAC, we have measured the in-situ conductivity of HgSe under high pressures up to 53GPa at room temperature, and investigated the temperature dependence of conductivity under several pressures. The result shows that the ZB HgSe exhibits the electrical property of a semimetal, characterized by the positive temperature slope of conductivity and a large conductivity. The conductivity decreases by four orders of magnitude at around 1.5GPa, corresponding to the transition from the ZB to the cinnabar structure. From 2 to 16GPa, the cinnabar HgSe exhibits the electrical property of a semiconductor, characterized by a positive temperature slope of conductivity. Within 16 to 18GPa, the conductivity increases abruptly by at least four orders of magnitude, corresponding to the transition from the cinnabar to the rocksalt structure. Another discontinuous change in conductivity is observed at around 49GPa. In comparison with HgTe, we speculate that HgSe may undergo a transition from the orthorhombic to a distorted CsCl structure at this pressure. Above 49GPa, the sample exhibits the electrical property of a conductor, characterized by a negative temperature slope of conductivity.

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