# THERMAL AND ELECTRICAL TRANSPORT STUDY ON THERMOELECTRIC MATERIALS THROUGH NANOSTRUCTURING AND MAGNETIC FIELD

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# THERMAL AND ELECTRICAL TRANSPORT STUDY ON THERMOELECTRIC MATERIALS THROUGH NANOSTRUCTURING AND MAGNETIC FIELD

#### MENGLIANG YAO

A dissertation

submitted to the Faculty of

the Department of Physics

in partial fulfillment

of the requirements for the degree of

Doctor of Philosophy

Boston College Morrissey College of Arts and Sciences Graduate School

June 2017

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#### Abstract

## Title: THERMAL AND ELECTRICAL TRANSPORT STUDY ON THERMOELECTRIC MATERIALS THROUGH NANOSTRUCTURING AND MAGNETIC FIELD

Author: Mengliang Yao

Advisor: Dr. Cyril P. Opeil, S.J. (Chair)

Committee Members: Dr. Michael J. Naughton, Dr. Krzysztof Kempa, and Dr. Mona Zebarjadi

Thermoelectric (TE) materials are of great interest to contemporary scientists because of their ability to directly convert temperature differences into electricity, and are regarded as a promising mode of alternative energy. The TE conversion efficiency is determined by the Carnot efficiency,  $\eta_{\rm C}$  and is relevant to a commonly used figure of merit *ZT* of a material. Improving the value of *ZT* is presently a core mission within the TE field. In order to advance our understanding of thermoelectric materials and improve their efficiency, this dissertation investigates the low-temperature behavior of the *p*-type thermoelectric Cu<sub>2</sub>Se through chemical doping and nanostructuring. It demonstrates a method to separate the electronic and lattice thermal conductivities in single crystal Bi<sub>2</sub>Te<sub>3</sub>, Cu, Al, Zn, and probes the electrical transport of quasi 2D bismuth textured thin films.

Cu<sub>2</sub>Se is a good high temperature TE material due to its phonon-liquid electron-crystal (PLEC) properties. It shows a discontinuity in transport coefficients and ZT around a structural transition. The present work on  $Cu_2Se$  at low temperatures shows that it is a promising *p*-type TE material in the low temperature regime and investigates the Peierls transition and charge-density wave (CDW) response to doping [1]. After entering the CDW ground state, an oscillation (wave-like fluctuation) was observed in the dc I-V curve near 50 K; this exhibits a periodic negative differential resistivity in an applied electric field due to the current. An investigation into the doping effect of Zn, Ni, and Te on the CDW ground state shows that Zn and Ni-doped Cu<sub>2</sub>Se produces an increased semiconducting energy gap and electron-phonon coupling constant, while the Te doping suppresses the Peierls transition. A similar fluctuating wave-like dc I-V curve was observed in Cu<sub>1.98</sub>Zn<sub>0.02</sub>Se near 40 K. This oscillatory behavior in the *dc* I-V curve was found to be insensitive to magnetic field but temperature dependent [2].

Understanding reducing thermal conductivity in TE materials is an important

facet of increasing TE efficiency and potential applications. In this dissertation, a magnetothermal (MTR) resistance method is used to measure the lattice thermal conductivity,  $\kappa_{ph}$  of single crystal Bi<sub>2</sub>Te<sub>3</sub> from 5 to 60 K. A large transverse magnetic field is applied to suppress the electronic thermal conduction while measuring thermal conductivity and electrical resistivity. The lattice thermal conductivity is then calculated by extrapolating the thermal conductivity versus electrical conductivity curve to a zero electrical conductivity value. The results show that the measured phonon thermal conductivity follows the  $e^{\Delta_{\min}/T}$  temperature dependence and the Lorenz ratio corresponds to the modified Sommerfeld value in the intermediate temperature range. These low-temperature experimental data and analysis on Bi<sub>2</sub>Te<sub>3</sub> are important compliments to previous measurements and theoretical calculations at higher temperatures, 100 - 300 K. The MTR method on Bi<sub>2</sub>Te<sub>3</sub> provides data necessary for first-principles calculations [4]. A parallel study on single crystal Cu, Al and Zn shows the applicability of the MTR method for separating  $\kappa_e$  and  $\kappa_{ph}$  in metals and indicates a significant deviation of the Lorenz ratio between 5 K and 60 K [3].

Elemental bismuth is a component of many TE compounds and in this dissertation magnetoresistance measurements are used investigate the effect of texturing

in polycrystalline bismuth thin films. Electrical current in bismuth films with texturing such that all grains are oriented with the trigonal axis normal to the film plane is found to flow in an isotropic manner. By contrast, bismuth films with no texture such that not all grains have the same crystallographic orientation exhibit anisotropic current flow, giving rise to preferential current flow pathways in each grain depending on its orientation. Textured and non-textured bismuth thin films are examined by measuring their angle-dependent magnetoresistance at different temperatures (3 – 300 K) and applied magnetic fields (0 – 90 kOe). Experimental evidence shows that the anisotropic conduction is due to the large mass anisotropy of bismuth and is confirmed by a parallel study on an antimony thin film [5].

- Mengliang Yao, Weishu Liu, Xiang Chen, Zhensong Ren, Stephen Wilson, Zhifeng Ren, and Cyril Opeil, J. Alloys Compd. 699, 718 (2017).
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- [4] Experimental determination of phonon thermal conductivity and Lorenz ratio of single crystal bismuth telluride, Mengliang Yao, Stephen Wilson, Mona Zebarjadi, and Cyril Opeil, under review.
- [5] Albert D. Liao, Mengliang Yao, Ferhat Katmis, Mingda Li, Shuang Tang, Jagadeesh S. Moodera, Cyril Opeil, Mildred S. Dresselhaus, Appl. Phys. Lett. 105, 063114 (2014).

Dedication

To my parents, paternal grandparents, and maternal grandparents

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#### Quotations

古今之成大事業、大學問者,必經過三種之境界:「昨夜西風凋碧 樹。獨上高樓,望盡天涯路。①」此第一境也。「衣帶漸寬終不悔,爲 伊消得人憔悴。②」此第二境也。「衆裏尋他千百度,驀然回首,那人 卻在,燈火闌珊處。③」此第三境也。此等語皆非大詞人不能道。然據 以此意解釋諸詞,恐爲晏歐諸公所不許也。

王國維《人間詞話》廿六

- (1) 晏殊《蝶戀花》:「檻菊愁煙蘭泣露。羅幕輕寒,燕子雙飛去。明月不諳離恨苦, 斜光到曉穿朱戶。昨夜西風凋碧樹。獨上高樓,望盡天涯路。欲寄彩箋兼尺素, 山長水闊知何處。」
- ② 柳永《鳳棲梧》:「佇倚危樓風細細。望極春愁, 黯黯生天際。草色煙光殘照裏。 無言誰會憑欄意。擬把疏狂圖一醉, 對酒當歌, 強樂無味。衣帶漸寬終不悔, 爲伊消得人憔悴。」
- ③ 辛棄疾《青玉案》(元夕):「東風夜放花千樹。更吹落、星如雨。寶馬雕車香滿路,鳳簫聲動,玉壺光轉,一夜魚龍舞。蛾兒雪柳黃金縷。笑語盈盈暗香去。 衆裏尋他千百度。驀然回首,那人卻在,燈火闌珊處。」

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Last and most importantly, my family, I am only able to finish my degree with your love and support. My mother has a joke on me that the time spending on the degree is approaching to the time against Japanese during the Second Sino-Japanese War (although it was expanded to 14 years recently due to the old time scale lacked the "Chapter 1 – Introduction"), and now it is done, thanks for your patience.

Mengliang Yao June 2017

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#### Chapter I: Introduction to Thermoelectric Effect

#### 1. Introduction

The thermoelectric (TE) effect is a direct conversion of temperature differences into electric voltage and vice versa. It is usually grouped into three categories of effects: the Seebeck effect, the Peltier effect and the Thomson effect. The first thermoelectric phenomenon was discovered by Thomas Johann Seebeck in 1821, and later described as "thermoelectricity" by Hans Christian Ørsted. Two related effects were discovered later, with the Peltier effect discovered by Jean Charles Athanase Peltier from experiments in 1834, and the Thomson effect discovered by William Thomson (Lord Kelvin) from theoretical predictions in 1851. Although these thermoelectric effects were discovered nearly 200 years ago, they have renewed researchers' interests in recent decades for the following reasons.

There is an increasing concern for global warming and an energy crisis nowadays. Currently, the majority of energy for human beings comes from fossil fuels, hydroelectric power, and nuclear power. Aside from these, there are some other minor clean energy sources which may be promising in the future, but have not developed much in the present, such as wind power, solar power, etc. Among the major energy resources, fossil fuels have been reported to be exhausted within 100 - 200 years. Meanwhile, plenty of greenhouse gases and contaminations are produced when making use of fossil fuels, and result in global warming and some relevant problems. Also plenty of the heat is wasted and not converted into electricity during the process. Hydroelectric energy is clean, but it strongly depends on natural circumstances, where one needs to have a suitable natural location first. Nuclear energy, more specifically nuclear fission energy, is argued to be dangerous and fatally toxic starting from its birth, especially after the emergences of the Chernobyl disaster and the Fukushima Daiichi nuclear disaster, which are both marked as level 7, *i.e.* major accident, in the International Nuclear Event Scale (INES). As a result, a clean, sustainable, non-location dependent energy form is needed, and thermoelectricity is a good candidate to meet the above demands as long as its conversion efficiency is high enough. Besides, thermoelectric material can also make use of the tremendous waste heat and convert it back into clean electric power. This makes it a very promising energy-saving material to overcome the vast energy gap in the future.

In this Chapter, the three fundamental thermoelectric principles will be

introduced, along with introduction of the thermoelectric performance of a TE unit with its optimization, and the transport coefficients with their temperature dependences.

#### 2. Seebeck Effect

The Seebeck effect was first observed by Baltic German physicist Thomas Johann Seebeck in 1821 [1-4]. He first reported the phenomenon that a compass needle would be deflected by a closed loop formed by two dissimilar metals joined in two places, with a temperature difference between the joints. First, he incorrectly called it the thermomagnetic effect. Later Hans Christian Ørsted recognized the current in the loop and changed the name to the thermoelectric effect, as shown in Fig. 1.1.



Fig. 1.1: Demonstration of the Seebeck effect, a circuit is formed from two dissimilar materials A and B, with different temperatures at two joints; the current is generated in the loop due to the thermal *emf* (electromotive force). Figure is taken from ref. [5].

The Seebeck effect is the direct conversion of heat into electricity at the junction of different materials, but the current or the closed loop is not necessary to describe the effect. From experiments, people found that the generated thermal *emf V*<sub>therm</sub> was proportional to the temperature difference  $\Delta T$  at two junctions:

$$V_{\text{therm}} = \int_{T_1}^{T_2} (S_{\text{B}} - S_{\text{A}}) \, \mathrm{d}T = S_{\text{BA}} \Delta T \tag{1.1}$$

Here,  $S_A$  and  $S_B$  are the absolute Seebeck coefficients and their difference  $S_{BA}$  is the relative Seebeck coefficient of two dissimilar materials A and B.

As mentioned above, even if there's only one material but with different temperatures at its two ends, there still exists the Seebeck effect. A thermal *emf* is generated from the temperature gradient inside the metal. From a phenomenological perspective, the Seebeck effect is very easily understood as follows. In an equilibrium state, there is no temperature gradient and thus  $\Delta T = 0$ . The free carriers are uniformly distributed in the system. However, if there is a temperature gradient, the free carriers begin to diffuse from the hot end into the cold end, and a thermal *emf* is established with an inner electric field preventing further diffusion, and forms a new equilibrium state. This generated *emf* V<sub>therm</sub> is proportional to the temperature difference  $\Delta T$  and the proportionality factor S is the absolute Seebeck coefficient of this material. Now the Seebeck coefficient S becomes an intrinsic property of the single material, where  $\Delta V$  is the voltage measured from experiments, as shown in Fig. 1.2 (*n*-type).

$$\Delta V = V_{\rm therm} = S \Delta T$$

(1.2)



Fig. 1.2: Illustration of the Seebeck effect of an *n*-type material. The electrons diffuse from the hot end to the cold end and a thermal *emf* is established. The inner electric field prevents more electrons from diffusing and a new equilibrium state is established. The illustration of a *p*-type material is similar.

#### 3. Peltier Effect

The Peltier effect is the second thermoelectric effect, first discovered in 1834 by French physicist Jean Charles Athanase Peltier [6], and states that when a current is made to flow through a junction between two dissimilar conductors A and B, heat Q may be released (or absorbed) at the junction depending on the direction of the current. The rate of heating or cooling, *i.e.* power P, is proportional to the current I going through the junction (from A to B):

$$P \equiv Q = (\Pi_{\rm A} - \Pi_{\rm B})I \tag{1.3}$$

where  $\Pi_A$  and  $\Pi_B$  are the Peltier coefficients of conductors A and B respectively.

According to Boltzmann transport theory, the presence of a current leads to the generation of a heat flux, because the free carriers not only transport charge but also transport heat. The electric current is continuous going through the junction because there's no leak of the current and for a single material its heat flux is proportional to its electric current but the ratio is material dependent. Thus, the heat flux will not be continuous through the junction if it is only transported along with the electric current. In order to prevent the discontinuity of the heat flux, extra released or absorbed heat is

needed at the junction, and that is the Peltier effect, as shown in Fig. 1.3.



Fig. 1.3: Demonstration of the Peltier effect. The electric current is driven by an external power source, the absorption or the liberation of the heat depends on the direction of the current going through the junction, *i.e.* from A to B or from B to A, as indicated by  $-\Delta T$  at the left joint and  $+\Delta T$  at the right joint. Figure is taken from ref. [5].

#### 4. Thomson Effect

The third thermoelectric effect, the Thomson effect, was first theoretically derived by Lord Kelvin in 1851 [7, 8], describing the heating or cooling of single current-carrying material with a temperature gradient. Usually the Seebeck coefficient is a function of temperature, so a spatial gradient in temperature can result in a gradient in the Seebeck coefficient. If a current is driven through this gradient, then a continuous version of the Peltier effect will occur. The power density p is described by the following formula where  $\vec{j}$  is the current density, and the proportional constant  $\kappa$  is called the Thomson coefficient:

$$p = -\kappa \bar{j} \cdot \nabla T \tag{1.4}$$

Similar to the Peltier effect, the absorption or liberation of heat also depends on the direction of the current and the thermal gradient, and can be categorized into positive or negative Thomson effect. Fig. 4 illustrates the positive Thomson effect.


Fig. 1.4: Positive Thomson effect. Heat is evolved when current is passed from hot end to the cold end when the current is anti-parallel to the thermal gradient, and vice versa. Figure is adopted from ref. [11].

## 5. Thomson Relations

In 1854, three years after the discovery of the Thomson effect, William Thomson discovered the relationship between the three thermoelectric effects: the Seebeck effect, the Peltier effect, and the Thomson effect [9, 10]. Their coefficients were related by the following two formulae, called the first Thomson relation (1.6) and the second Thomson relation (1.5):

$$\Pi = TS$$
(1.5)
$$\kappa = T \frac{\mathrm{d}S}{\mathrm{d}T} = \frac{\mathrm{d}\Pi}{\mathrm{d}T} - S$$

(1.6)

As a result, these three thermoelectric effects are related. In other words, there's only one independent thermoelectric effect, which was chosen to be the Seebeck effect. The reason is from the experimental considerations. Among the three effects, aside from the Seebeck effect, the other two effects need a steady current going through the material to perform the caloric measurements. The heat measurements do not have the same level of precision as the voltage measurements of the Seebeck effect, and also need much more complicated experimental setups compared with the latter one.

# 6. Figure of Merit

From the previously introduced three thermoelectric effects, it is naturally realized that the temperature differences can be used to produce electricity through the Seebeck effect. Meanwhile, a refrigerator can be created just by applying a current according to the Peltier effect, as shown in Fig. 1.5 [12-14]. Then, a very important question comes out: What is the efficiency of those apparatuses when they are converting the heat into electricity and vice versa, or more directly what is the efficiency of thermoelectric materials?



Fig. 1.5: The diagram on the left is power generation according to the Seebeck effect, while the diagram on the right is a refrigerator according to the Peltier effect. Figures are taken from ref. [14].

Normally, in order to achieve a higher efficiency, the *n*-type and *p*-type semiconducting materials are used together as a pair in a setup, and the efficiencies are given by the following expressions, where  $\phi$  is the coefficient-of-performance (COP) of a refrigerator and  $\eta$  the TE efficiency of a thermoelectric generator [5]:

$$\phi = \frac{T_{\rm c}}{T_{\rm h} - T_{\rm c}} \frac{\sqrt{1 + ZT} - \frac{T_{\rm h}}{T_{\rm c}}}{\sqrt{1 + ZT} + 1} = \frac{(1 - \eta_{\rm C})\sqrt{1 + ZT} - 1}{\eta_{\rm C}(\sqrt{1 + ZT} + 1)}$$
(1.7)

$$\eta = \frac{T_{\rm h} - T_{\rm c}}{T_{\rm h}} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_{\rm c}}{T_{\rm h}}} = \frac{\eta_{\rm C} (\sqrt{1 + ZT} - 1)}{\sqrt{1 + ZT} + 1 - \eta_{\rm C}}$$
(1.8)

Here,  $T_c$  and  $T_h$  are the temperatures at the cold and hot reservoirs respectively,  $T \equiv \frac{T_h + T_c}{2}$  is the average temperature,  $\eta_c \equiv 1 - \frac{T_c}{T_h}$  is the Carnot efficiency, and ZT is the dimensionless figure of merit, defined by

$$ZT \equiv \frac{\left(S_{\rm p} - S_{\rm n}\right)^2 T}{\left(\sqrt{\kappa_{\rm p}\rho_{\rm p}} + \sqrt{\kappa_{\rm n}\rho_{\rm n}}\right)^2}$$
(1.9)

Here, subscripts p and n represent the p-type and n-type leg respectively, and S,  $\kappa$ ,  $\rho$  are the Seebeck coefficient, thermal conductivity and electrical resistivity. Correspondingly, the dimensionless figure of merit of single thermoelectric material zT

is defined as

$$zT \equiv \frac{S^2T}{\kappa\rho}$$

(1.10)

According to thermodynamics, the highest efficiency one could get from an ideal heat engine is the Carnot efficiency  $\eta_{\rm C}$ . As a result, the efficiency from thermoelectric generation  $\eta$  must be less than  $\eta_{\rm C}$ , as verified by expression (1.8). Further, the efficiency only depends on two quantities: the Carnot efficiency  $\eta_{\rm C}$  and the dimensionless figure of merit *ZT*. The Carnot efficiency depends on the process of using and is material independent; however, figure of merit *zT* is a pure material dependent quantity and is the one really representing the quality of a thermoelectric material.



Fig. 1.6: Ratio of the thermoelectric efficiency to the Carnot efficiency, which depends on the Carnot efficiency itself and also the material dependent dimensionless figure of merit. The right figure is plotted when the Carnot efficiency is  $\frac{5}{8}$ .

Fig. 1.6 illustrates the dependence of the thermoelectric generation efficiency  $\eta$  with respect to its two arguments: the Carnot efficiency  $\eta_C$  and the dimensionless figure of merit zT. As we see,  $\eta$  monotonously increases with respect to the increase of  $\eta_C$  and zT, and the contribution is mainly from zT. Thus, to find a good thermoelectric material with a large zT value is very important. The right figure in Fig. 1.6 shows the efficiency curve at a selected Carnot efficiency. When zT equals 2, the efficiency approaches 35%, while when zT comes to 4, the efficiency is near 50%. It is considered only when the figure of merit is larger than 4 the thermoelectric materials become applicable. Thus, the present-day most promising bulk TE material, single crystal SnSe [15], having a zT of 2.5, is still far away from real application, if we only consider the thermoelectric performance itself.

#### 7. Electrical Resistivity

The electrical resistivity describes how strongly a material opposes the flow of electric current under an applied electric field. However, in transport theory, it is more convenient to use electrical conductivity to set up the theoretical framework, where the electrical conductivity tensor  $\hat{\sigma}$  is the coefficient relating the vector electric field  $\vec{E}$  to

the vector current density  $\vec{j}$ :

$$\vec{j} = \hat{\sigma}\vec{E}$$
(1.11)

The electrical resistivity tensor  $\hat{\rho}$  is defined as the matrix inverse of the electrical conductivity tensor  $\hat{\sigma}$ . Starting from the Boltzmann transport equation in the relaxation-time approximation, where  $\tau$  is the relaxation time and  $\vec{v}$  is the electron velocity [16]:

$$\frac{\partial f(\vec{r},\vec{k},t)}{\partial t} + \vec{v} \cdot \nabla_{\vec{r}} f(\vec{r},\vec{k},t) + \vec{F} \cdot \frac{1}{\hbar} \nabla_{\vec{k}} f(\vec{r},\vec{k},t) = -\frac{f(\vec{r},\vec{k},t) - f_0(\vec{k})}{\tau(\vec{k})}$$
(1.12)

Here  $f(\vec{r}, \vec{k}, t)$  is the nonequilibrium charge carrier distribution function, while  $f_0(\vec{k})$ is its local equilibrium form, *i.e.* the Fermi distribution  $f_0(\vec{k}) = \frac{1}{\exp\left(\frac{\epsilon(\vec{k})-\mu}{k_{\rm B}T}\right)+1}$ . The

electrical conductivity can be expressed as the sum of contributions from each energy band [16]:

$$\hat{\sigma}(\omega) = \sum_{n} \hat{\sigma}^{(n)}(\omega) = \sum_{n} e^{2} \int \frac{\mathrm{d}^{3}k}{4\pi^{3}} \frac{\vec{v}_{n}(\vec{k})\vec{v}_{n}(\vec{k})(-\partial f/\partial\epsilon)_{\epsilon=\epsilon_{n}(\vec{k})}}{\left[1/\tau_{n}(\epsilon_{n}(\vec{k}))\right] - \mathrm{i}\omega}$$
(1.13)

In the free electron model, with the assumption of the same relaxation time  $\tau$ , the electrical conductivity tensor reduces to a scalar with the value of  $\sigma = \frac{ne^2\tau}{m^*}$ , where *n*  is the band index and  $m^*$  is the effective mass of the carrier. The result is recovered from the Drude model, except the free electron mass is replaced by its effective mass. If we define mobility as  $\mu = \frac{e\tau}{m^*}$  then we obtain:

$$\sigma = n e \mu \tag{1.14}$$

This is a general expression to estimate the mobility of a simple material from electrical resistivity and Hall coefficient measurements. In semiconductors, the formula needs to be modified as follows, due to the coexistence of both electrons and holes:

$$\sigma = e(n_{\rm e}\mu_{\rm e} + n_{\rm h}\mu_{\rm h}) \tag{1.15}$$

### 8. Thermal Conductivity

Similar to the electrical conductivity, the thermal conductivity is defined as the coefficient relating the temperature gradient  $\nabla T$  to the heat flux  $\vec{q}$ 

$$\vec{q} = -\hat{\kappa} \nabla T \tag{1.16}$$

In principle, the thermal conductivity  $\hat{\kappa}$  also behaves as a tensor like the

electrical conductivity  $\hat{\sigma}$ . However, due to the complexity of thermal transport measurements, it is very hard to perform thermal Hall measurements, *i.e.* measuring  $\kappa_{yx}$ or other off-diagonal components. Most thermal transport measurements are performed to get  $\kappa_{xx}$  (or  $\kappa_{yy}$ ), so to some extent the thermal conductivity tensor  $\hat{\kappa}$  reduces to a thermal conductivity scalar  $\kappa$ . In the following description in this Chapter, the terms "phonon(s)" and "lattice" are interchangeable with one another.

Unlike electrical conduction, which usually conducts only by electrons in normal cases, the thermal conduction always conducts by both electrons and phonons. Indeed, there are some cases, for example, the Cooper pair, which exists in the superconducting state of superconductors, that only conduct charge but do not conduct heat (or entropy). However, as for superconductors themselves, because their lattice still conducts heat no matter if it is in or out of the superconducting state, they still have a finite thermal conductivity. Therefore, the total thermal conductivity  $\kappa_{tot}$  is given as the sum of two components by [17]:

$$\kappa_{\rm tot} = \kappa_{\rm carrier} + \kappa_{\rm ph}$$
(1.17)

where  $\kappa_{ph}$  is the phonon contribution while  $\kappa_{carrier}$  is the contributions from free

carriers, such as electrons, holes, etc. For semiconductors, both electrons and holes contribute to the thermal conductivity and  $\kappa_{carrier}$  is given by [17]:

$$\kappa_{\text{carrier}} = \kappa_{\text{e}} + \kappa_{\text{h}} + \frac{\sigma_{\text{e}}\sigma_{\text{h}}}{\sigma_{\text{e}} + \sigma_{\text{h}}} (S_{\text{e}} - S_{\text{h}})^2 T$$
(1.18)

where the  $3^{rd}$  term in (1.18) is conventionally called the bipolar contribution, which manifests itself at temperatures near or exceeding the energy of the band gap of the semiconductor due to thermal excitation. As a result, at low temperatures where thermal excitation is tiny, the bipolar effect is negligible. Henceforth, the thermal conductivity is focused on the  $\kappa_e$  (or  $\kappa_h$ ) and  $\kappa_{ph}$  parts.

The derivation of the electronic thermal conductivity  $\kappa_{\rm e}$  (or  $\kappa_{\rm h}$ , which will be omitted if there's no ambiguity) is similar to the derivation (1.12) of electrical conductivity  $\sigma$  where we start from the Boltzmann transport equation in the relaxation time approximation, where  $\vec{v}(\vec{k})$ , *T*, and  $\vec{E}$  are the electron velocity, the absolute temperature, and the electric field, respectively [18,19]:

$$\vec{v}(\vec{k}) \cdot \left(\frac{\partial f(\vec{r},\vec{k},t)}{\partial T} \nabla T + e \frac{\partial f(\vec{r},\vec{k},t)}{\partial \epsilon(\vec{k})} \vec{E}\right) = -\frac{f(\vec{r},\vec{k},t) - f_0(\vec{k})}{\tau(\vec{k})}$$
(1.19)

If we define a general integral  $K_n$  as [18]

$$K_n \equiv -\frac{1}{3} \int \vec{v}^2(\vec{k}) \tau(\vec{k}) (\epsilon(\vec{k}) - \epsilon_{\rm F})^n \frac{\partial f_0(\vec{k})}{\partial \epsilon(\vec{k})} \mathrm{d}^3 k$$
(1.20)

then the electronic thermal conductivity  $\kappa_e$  and electrical conductivity  $\sigma$  can be expressed as

$$\kappa_{\rm e} = \frac{1}{T} \left( K_2 - \frac{K_1^2}{K_0} \right) \tag{1.21}$$

$$\sigma = e^2 K_0$$

(1.22)

The detailed expressions of (1.21) and (1.22) are different for different electron involved scattering processes because they have different relaxation times.

For phonons, we also start from the Boltzmann transport equation in the relaxation-time approximation. However, because phonons are bosons without charge, the equation is written as [18,19]

$$\left(\vec{v}_{g} \cdot \nabla T\right) \frac{\partial \mathcal{N}(\vec{r}, \vec{q}, t)}{\partial T} = -\frac{\mathcal{N}(\vec{r}, \vec{q}, t) - \mathcal{N}_{0}(\vec{q})}{\tau(\vec{q})}$$
(1.23)

where  $\vec{v}_{g}$  is the phonon group velocity and  $\mathcal{N}_{0}(\vec{q}) = \frac{1}{\exp(\frac{\hbar\omega(\vec{q})}{k_{\mathrm{B}}T})-1}$  is the Bose

distribution when the phonons are in their equilibrium. The phonon thermal conductivity

 $\kappa_{\rm ph}$  can be expressed as [18,19]

$$\kappa_{\rm ph} = \frac{1}{3} \int \hbar \omega(\vec{q}) \vec{v}_{\rm g}^2 \tau(\vec{q}) \frac{\partial \mathcal{N}_0(\vec{q})}{\partial T} \frac{3q^2}{2\pi^2} dq$$
(1.24)

Both  $\kappa_e$  and  $\kappa_{ph}$  share a similar relationship between thermal conductivity and specific heat (heat capacity per unit volume) [16,18,19]

$$\kappa = \frac{1}{3}c_{\nu}\nu^{2}\tau = \frac{1}{3}c_{\nu}\nu l$$
(1.25)

where  $c_v$  is the specific heat, v is the velocity,  $\tau$  is the relaxation time, and l is the mean free path.

#### 9. Seebeck Coefficient

Unlike electrical conductivity ( $\sigma$ ) and thermal conductivity ( $\kappa$ ), the existence of Seebeck effect does not need an electric current  $\vec{j}$  or a dissipative energy flux  $\vec{q}'$  (the prime notation here is a direct quotation from Landau's vol. 10 ref. [20]). However, the Seebeck coefficient *S* is related to  $\sigma$  (or  $\rho$ ) and  $\kappa$  through the following transport equations [20,21], note that temperature gradient  $\nabla T$  is a vector:

$$\vec{E} + \nabla \left(\frac{\mu}{e}\right) = \rho \vec{j} + S \nabla T$$

(1.26)

$$\vec{q}' = ST\vec{j} - \kappa \nabla T \tag{1.27}$$

where  $\mu$  and e are the chemical potential and the electron charge, respectively.

The Seebeck coefficient can be derived for an isotropic model of a metal under the assumption of elastic collisions, which is called Mott's formula [18,21,22]:

$$S = \frac{\pi^2 k_{\rm B}^2 T}{3e} \frac{\partial \log(\sigma(\epsilon))}{\partial \epsilon} \Big|_{\epsilon = \epsilon_{\rm F}}$$
(1.28)

If we deal with free electrons scattered from impurities, which happens at the residual resistance range when temperature becomes sufficiently low, the Seebeck coefficient is estimated as follows [22], from which we can see the Seebeck coefficient of metals is usually very small and can be neglected:

$$S = \frac{\pi^2 k_{\rm B} k_{\rm B} T}{3e} \sim 10^{-8} \times T \ \text{V/K} = 10^{-2} \times T \ \mu\text{V/K}$$
(1.29)

Eqn. (1.28) can be written in terms of carrier concentration n and mobility  $\mu$  as [22]:

$$S = \frac{\pi^2 k_{\rm B}^2 T}{3e} \left[ \frac{1}{n} \frac{\partial n(\epsilon)}{\partial \epsilon} + \frac{1}{\mu} \frac{\partial \mu(\epsilon)}{\partial \epsilon} \right]_{\epsilon = \epsilon_{\rm F}}$$

The Seebeck coefficient in the degenerate limit for a single parabolic band can be

expressed as [22]:

$$S = \frac{k_{\rm B}}{e} \frac{(r+5/2)F_{r+3/2}(\xi)}{(r+3/2)F_{r+1/2}(\xi)} - \xi$$
(1.31)

where  $F_n(\xi)$  is the Fermi integral defined by

$$F_n(\xi) = \int_0^{+\infty} \frac{\chi^n}{1 + e^{\chi - \xi}} d\chi$$

r and  $\xi \equiv {\epsilon_F / k_B T}$  are the scattering parameter and the reduced Fermi energy, respectively.

Just as in electrical conductivity and thermal conductivity, if there exist two types of carriers, the total Seebeck coefficient is the contribution of both carriers, but not in a direct sum

$$S = \frac{S_{\rm e}\sigma_{\rm e} + S_{\rm h}\sigma_{\rm h}}{\sigma_{\rm e} + \sigma_{\rm h}}$$
(1.33)

In discussing thermoelectric quantities and characterization, it is important to link them with the underlying physics concepts and thermodynamics. If one considers the

(1.32)

dimensionality of the Seebeck coefficient, its unit is V/K (in thermoelectricity  $\mu$ V/K is more commonly used), so its dimension (in SI units) is  $[S] = \left[\frac{\text{voltage}}{\text{temperature}}\right] = \left[\frac{V}{K}\right] = \frac{L^2 M T^{-3} I^{-1}}{\Theta} = L^2 M T^{-3} I^{-1} \Theta^{-1}$ . We know that the entropy is defined as  $dS = \frac{\delta Q}{T}$  thus its dimension is  $[S] = \left[\frac{\text{heat}}{\text{temperature}}\right] = \left[\frac{\text{energy}}{\text{temperature}}\right] = \left[\frac{\text{charge} \times \text{voltage}}{\text{temperature}}\right] = L^2 M T^{-2} \Theta^{-1}$ , as a result  $[S] = \left[\frac{\delta}{Q}\right]$  where *S*, *S*, and *Q* are the Seebeck coefficient, entropy, and electric charge respectively. From this analysis one can see that the most fundamental description of the Seebeck coefficient is a consideration of entropy per charge. Thus a large thermoelectric effect or Seebeck coefficient quantifies a large entropy per charge carrier for the system.

#### 10. Wiedemann-Franz Law

The Wiedemann-Franz law, or in short the W-F law, states that the ratio of the thermal conductivity  $\kappa$  to the electrical conductivity  $\sigma$  of a metal is proportional to the absolute temperature *T*. Gustav Wiedemann and Rudolph Franz reported that  $\kappa/\sigma$  has approximately the same value for different metals at the same temperature in 1853 [23], and Ludvig Lorenz discovered the proportionality of  $\kappa/\sigma$  with temperature in 1872. The proportionality constant is called the Lorenz number *L* and its value for a free electron

gas is called the Sommerfeld value of the Lorenz number  $L_0$  and equals [16,18-21]

$$L_0 = \frac{\pi^2}{3} \left(\frac{k_{\rm B}}{e}\right)^2 = 2.443 \times 10^{-8} \ {\rm V}^2 / {\rm K}^2$$
(1.34)

Note that the Lorenz number has a dimension of  $S^2$ .

Strictly speaking, the thermal conductivity used to extract the Lorenz number is the electronic thermal conductivity  $\kappa_{e}$ , but due to the overwhelming electronic transport in metals, the above descriptions are still accurate enough without large deviations. Besides, every material has its own thermoelectric effect, no matter how large or small. As a result, if the thermoelectric term is considered, the real Lorenz number will deviate from the Sommerfeld value by a little bit [20]

$$L \equiv \frac{\kappa_{\rm e}}{\sigma T} = L_0 - S^2 \tag{1.35}$$

Normally the Seebeck coefficient of metals is on the order of several  $\mu V/K$  and thus can be omitted safely in (1.35). But for semiconductors, the Seebeck coefficient is usually up to several hundred  $\mu V/K$  and needs to be taken into account. The Lorenz number also depends on the temperature. It approaches its Sommerfeld value at lowest residual resistance temperature range and around or above room temperature range, where electron-impurity scattering and electron-phonon scattering are elastic and become dominant, respectively [18].

### 11. Temperature Dependence of Transport Coefficients

There's no doubt that all of the transport coefficients  $\kappa$ ,  $\sigma$  and S are generally temperature dependent, and as a result, the derived figure of merit  $zT = \frac{S^2T}{\kappa\rho}$  is also temperature dependent. In this section, I will briefly organize some contents on their temperature behaviors below room temperatures, especially in the low temperature range.

Electrical conductivity  $\sigma$  is easier to deal with than thermal conductivity  $\kappa$ , since only electrons conduct charge. As a result, people only need to deal with the scattering between electrons and other particles or quasi-particles, such as phonons, electrons, defects, dislocations, boundaries, etc. However, for thermal conductivity, we need to consider both electrons and phonons, *i.e.* the electronic thermal conductivity  $\kappa_{e}$ and phonon thermal conductivity  $\kappa_{ph}$ , separately.

The Debye temperature  $\Theta_{\rm D} \equiv \frac{\hbar\omega_{\rm max}}{k_{\rm B}}$  is used to characterize the level of the temperature, *i.e.* if  $T \ll \Theta_{\rm D}$  it is said T is in the low temperature range, while if

 $T \gg \Theta_D$  then it is said *T* is in the high temperature range. For most of the materials, room temperature is in the high temperature range.

When  $T \gg \Theta_{\rm D}$  the dominant scattering mechanism is the high temperature electron-phonon scattering. Phonons with all possible quasi-momenta are excited in the crystal up to the maximum value, with the same order of magnitude as the electron Fermi momentum, thus enabling us to treat phonon emission or absorption approximately as elastic scattering of an electron [20]. When considering  $\kappa_{\rm ph}$ , there are mainly two dominant scattering mechanisms: one is the phonon-phonon Umklapp-process at high temperatures and  $\kappa_{\rm ph}^{\rm ph}$  is used to designate the lattice thermal conductivity from this mechanism, and the other is the lattice thermal conductivity from the phonon-electron scattering designated as  $\kappa_{\rm ph}^{\rm eh}$  [18-20]. It is concluded that at this temperature range:

- 1.  $\rho \sim T$ ;
- 2.  $\sigma = 1/\rho \sim 1/T;$
- 3.  $\kappa_{\rm e}$ ~const;
- 4.  $\kappa_{\rm ph}^{\rm ph} \sim 1/_T;$
- 5.  $\kappa_{\rm ph}^{\rm e} \sim {\rm const.}$

We see that  $\kappa_e/\sigma \sim T$  and satisfies the W-F law. This is because the electron-phonon

scattering is elastic. Due to the fact that in metals  $\kappa_e \gg \kappa_{ph}$ , what we observe at room temperature is that most of the metals obey the W-F law.

In the intermediate temperature range, the mechanism is complicated because of lacking the asymptotic power law expressions of the formulae. However, in this temperature range, the electron-phonon scattering is still dominant. When temperature even goes lower, where  $T \ll \Theta_D$ , which is referred to as low temperature range but not that ultra-low, the situation becomes simple due to the existence of simple asymptotic expressions for electron-phonon scattering again. It is concluded that [18-20]:

- 1.  $\rho \sim T^5$  (Bloch's  $T^5$  law);
- 2.  $\sigma = 1/\rho \sim T^{-5};$
- 3.  $\kappa_{\rm e} \sim T^{-2}$ ;
- 4.  $\kappa_{\rm ph}^{\rm ph} \sim e^{\Delta_{\rm min}/T};$
- 5.  $\kappa_{\rm ph}^{\rm e} \sim T^2$ .

At this temperature range the W-F law no longer holds, as we see from the estimation  $\kappa_{\rm e}/_{\sigma} \sim T^3$ .

When temperature goes even lower, the electron-phonon collision frequency decreases and ultimately the collisions between electrons and impurities become predominant in causing the electrical and thermal resistance in metals, and this is the residual resistance range. Also, there may exist the scatterings between electron and electron above the residual resistance range. For the thermal conductivity, according to (1.25), at the lowest temperature the velocity v and mean free path l become constants and the  $\kappa$ 's behavior purely comes from specific heat  $c_v$ . Thus [18-20]

- 1.  $\rho^{s-s} \sim T^2$  (normal electron-electron scatterings, *i.e.* s-electron scatterings);
- 2.  $\rho^{s-d} \sim T^3$  (s-d electron scatterings for transition metals);
- 3.  $\rho^{\text{res}}$ ~const ("res" stands for "residual");
- 4.  $\sigma^{\rm res} = 1/\rho^{\rm res} \sim {\rm const};$
- 5.  $\kappa_{\rm e}^{\rm s-s} \sim 1/_T;$
- 6.  $\kappa_{\rm e}^{\rm res} \sim T$ ;
- 7.  $\kappa_{\rm ph}^{\rm res} \sim T^3$ .

Due to the existence of impurities and the fact that the scatterings are elastic, the W-F law is recovered, as we see  $\frac{\kappa_e^{\text{res}}}{\sigma^{\text{res}}} \sim T$ . Combined with the temperature behavior of Seebeck coefficient at low temperature eqn. (1.29), we are able to extract that the figure of merit always approaches zero at low temperatures, if we assume that  $\kappa_{\text{tot}} = \kappa_e + \kappa_{\text{ph}} \sim \gamma T + \delta T^3$  then

$$\lim_{T \to 0} zT \sim \frac{T^2}{\gamma + \delta T^2} \to 0$$
(1.36)

### 12. Optimization of Figure of Merit

From the definition of figure of merit  $zT = \frac{S^2T}{\kappa\rho}$  we can see that besides it being temperature dependent, its value also depends on all three transport coefficients [24]:

- 1. Large Seebeck coefficient *S* means large open circuit voltage for generators, also large Peltier coefficient  $\Pi = TS$  for refrigerators;
- 2. Low thermal conductivity  $\kappa$  means it is easier to maintain temperature gradient for generators and reduce heat conducting back to cold side for refrigerators;
- 3. High electrical conductivity  $\sigma$  or low electrical resistivity  $\rho$  means low Joule heating.

All of the three factors are important to achieve a high zT material. However, these three quantities are highly correlated and it is hard to just only tune one factor but leave others slightly altered [24]:

1. Increasing carrier concentration n will increase  $\sigma$  but reduce S;

- 2. Increasing effective mass will increase S but decrease mobility  $\mu$  and  $\sigma$ ;
- 3. Increasing  $\sigma$  will increase  $\kappa_e$  (Wiedemann-Franz Law);
- 4. Decreasing  $\kappa_{ph}$  by adding defects will decrease mobility  $\mu$  and  $\sigma$ .

However, generally speaking, all of the transport coefficients are actually functions of carrier concentration n, as shown in Fig. 1.7 [25,26]. The carrier concentration is plotted in *log* scale, where both  $\kappa$  and  $\sigma$  increase with increasing n, but the Seebeck coefficient has the opposite trend. As a result, the figure of merit has a maximum in the middle range of the carrier concentration, and it usually locates in the range of heavily doped semiconductors.



Fig. 1.7: Demonstration of the relations between the transport coefficients and carrier concentration for a bulk material. Good thermoelectric materials are typically heavily doped semiconductors with a carrier concentration between  $10^{19}$  and  $10^{21}$  carriers per cm<sup>3</sup>. Trends shown here were modeled from Bi<sub>2</sub>Te<sub>3</sub>. Figure is taken from ref. [25].

Starting in the 1950s, people began to search for high zT materials until they found Bi<sub>2</sub>Te<sub>3</sub> and its alloys with Sb and Se, which have a zT value around 1. There were very limited improvements on good quality single crystal bulk materials during the following several decades [12,26,29,30]. The sudden increase of figure of merit during the 1990s was due to the introduction of nanostructures in the bulk, which was first indicated by Hicks and Dresselhaus in 1993 [27,28]. Fig. 1.8 shows the improvement trajectory of  $zT_{max}$  from 1950s to 2000s. We can see that after 1970, because of a lack of new theories, the increase of figure of merit is negligible, until the work of Hicks and Dresselhaus.



Fig. 1.8: Evolution of the maximum *zT* over time. Materials for thermoelectric cooling are shown as blue dots and for thermoelectric power generation as red triangles. The black dashed line guides the eye. Figure is taken from ref. [29].

Nowadays, in order to explore high figure of merit material, people basically adopt the following approaches [24,26]:

- Unusual band structures, such as heavy fermion compounds, which have large Seebeck coefficient;
- Phonon glass electron crystal (PGEC), such as skutterudites, clathrates, and β-Zn<sub>4</sub>Sb<sub>3</sub>, which exhibit pretty good electrical conduction and poor phonon thermal conduction due to their controlled disorder;
- Quantum confined structures, such as 2-D superlattices, 1-D nanowires and nanocomposites, which have large Seebeck coefficient and low phonon thermal conductivity.

Nanocomposites, made by mechanical ball milling and hot pressing processes, are one of the best and most economic approaches to further improve the thermoelectric performance of a good thermoelectric material. From Fig. 1.8 we can see the power of nanocomposites. The zT value of Bi<sub>2</sub>Te<sub>3</sub> increased from 1 in the single crystal to 1.5 in the nanocomposites. The intrinsic reasoning of this improvement comes from two aspects:

1. The mean free path of phonons  $l_{ph}$  is normally much greater than the one of

electrons  $l_e$ . At the lowest temperatures, the mean free path of phonons may be on the order of millimeters [19], which is the size of some small specimens. When introducing the nanostructures, *i.e.* the nanoscale grains, whose sizes D are in between of the mean free path of electrons and phonons:

$$l_{\rm e} < D < l_{\rm ph} \tag{1.37}$$

So the phonons will be strongly scattered by the grain boundaries, as shown in Fig. 1.9, while electrons are slightly affected. As a result  $\kappa_{ph}$  is significantly depressed while leaving  $\kappa_{e}$  and  $\sigma$  altered a little bit and still good enough.



Fig. 1.9: Schematic illustration of grain boundary scattering mechanism. Phonon are scattered by the boundaries, and phonon thermal conduction is reduced. Figure is taken from author's 2014 APS March meeting.

2. Due to the nanoscale grains, quantum confinement may also take effect, and increase the Seebeck coefficient and tune S and  $\rho$  independently to increase the power factor.

Just as mentioned in section 6, figure of merit is material dependent. It is also temperature dependent. As a result, the maximum of the zT curve determines the temperature range in which a thermoelectric material is best suitable. Fig. 1.10 shows a representative zT plot of different materials from low temperature to high temperature [25,26,31]. From the figure we see that the highest figure of merit is from the superlattices, due to their quantum confinement. However, it is very hard to assemble them into practical usage, because a huge efficiency lost will occur in the conjunction part and lower the total figure of merit of the thermoelectric unit to an unpractical level.

Besides having a high zT value, a good thermoelectric material must be in the solid state and compositionally stable, or even earth abundant and nontoxic. The original application of thermoelectric material is in the deep space project, when the solar cell cannot convert enough electricity because far away from the Sun, the combination of radioactive heat source and thermoelectric unit is able to supply the spacecraft energy as needed for a foreseeable period of time. As a result the solid state and stability must be satisfied. However, when taking into account the daily practical use, the nontoxic

property cannot be absent. In order to lower the price, the composition from earth abundant elements is also needed. All of the above factors determine or guide a thermoelectrically efficient, affordable, chemically safe, long lasting bulk and solid state thermoelectric material, and as a very promising clean energy saving material.



Fig. 1.10: Non-dimensional figure of merit zT as a function of temperature for state of the art materials. Figure is taken from ref. [31].

#### 13. Thermodynamics and Thermoelectricity

This section is a brief introduction on the basis of thermodynamics and its relevance to the thermoelectricity. The contents are mainly based on chapter 2 of ref. [22], as well as partially refered to ref. [32].

The thermodynamics is based on the four laws of thermodynamics:

0. The zeroth law of thermodynamics: If two systems are each in thermal equilibrium with a third, they are also in thermal equilibrium with each other.

$$T_{A} = T_{B}$$
  
 $T_{B} = T_{C}$ 
 $\Rightarrow T_{A} = T_{C}$ 

$$(1.38)$$

 The first law of thermodynamics: The increase in internal energy of a closed system is equal to total of the energy added to the system. It is a version of the law of conservation of energy, adapted for thermodynamic systems.

$$\mathrm{d}U = \delta Q - \delta W + \mu \mathrm{d}n$$

(1.39)

where dU is a change in internal system energy,  $\delta W$  is work performed by the system against external forces,  $\mu$  is system chemical potential, and dn is a change in the number of particles in the system.

 The second law of thermodynamics: The total entropy of an isolated system can only increase over time. It can remain constant in ideal cases where the system is in a steady state (equilibrium) or undergoing a reversible process.

$$T\mathrm{d}\mathcal{S} \ge \delta Q \tag{1.40}$$

where the equality sign is related to reversible and non-equality sign to irreversible processes (*i.e.* nonequilibrium processes such as heat transfer and electric current flow). T is absolute temperature and dS is total differential of state function entropy S.

 The third law of thermodynamics: The entropy of a perfect crystal at absolute zero is exactly equal to zero.

$$\mathcal{S}(0) = 0 \tag{1.41}$$

The conclusion of zero entropy is a consequence from quantum mechanics for a perfect crystal (residual entropy may still exist at absolute zero temperature, *e.g.* glass, one type of amorphous solids). In classical thermodynamics its value is undetermined.

A real thermal process is always an irreversible nonequilibrium process; as a result nonequilibrium thermodynamics is required for the description of thermoelectricity. There are mainly two approaches; one was introduced by Onsager in 1931, based on his assumption of minimum energy dissipation, as well as the detailed balance. The other was made by Prigozhin in 1947 on the assumption of minimum entropy production, which was proved more convenient for the solution of practical tasks than Onsager's approach. Both of their approaches deploy the local equilibrium *ansatz*, *i.e.* although the whole system is in a nonequilibrium state, it can be split into elementary volumes, which are microscopically small to the whole system but macroscopically large to the molecules they contain, such that each of them is actually in the equilibrium state individually.

As a result, besides the law of conservation of energy for volume elements (first law of thermodynamics), one still needs the following entropy balance equation:

$$\rho \frac{\mathrm{d}s}{\mathrm{d}t} = -\mathrm{div}\,\vec{J} + \sigma \tag{1.42}$$

where *s* is the entropy of volume unit,  $\vec{J}$  is entropy flow density expressed in terms of heat flow density, diffusion density, and part of stress tensor related to nonequilibrium processes (*i.e.* in terms of elastic stress tensor  $\Pi_{\alpha\beta}$ ),  $\sigma$  is unit local entropy production
per unit time expressed as following by considering the phenomenological equations (*i.e.* the equations relating fluxes with forces by transport coefficients):

$$\sigma = \sum_{ik} X_i L_{ik} X_k \ge 0 \tag{1.43}$$

where  $\vec{X}$  and  $\hat{L}$  are thermodynamic forces and transport (kinetic) coefficients, respectively.

Prigozhin's theorem states that in steady-state the value of  $\sigma$  is minimum under assigned external conditions preventing from establishment of equilibrium, *i.e.* in the state of thermodynamic equilibrium  $\sigma = 0$ .

Combine the first and second law of thermodynamics as well as the local equilibrium *ansatz* the basic equation of thermodynamics for quasi-static processes is

$$dU = TdS - \delta W + \sum_{r} \mu_{r} dn_{r}$$
(1.44)

and Onsager reciprocal relations still hold true for transport coefficients

$$L_{ik}(\vec{B}) = L_{ki}(-\vec{B})$$
(1.45)

where  $\vec{B}$  is magnetic induction vector.

Eqns. (1.26) and (1.27) are the generalized Ohm's law and Fourier's law respectively by considering the thermoelectric terms, because the Seebeck coefficient *S* is not a transport coefficient, it does not satisfy the functional form of eqn. (1.45). Compared with transport coefficients such as  $\rho$  or  $\kappa$ , which directly relates the forces with fluxes, the Seebeck coefficient or Peltier coefficient relates one force with another flux, *i.e.* it is a second order effect, thus its value is usually small and cannot be neglected safely, such as in the case of metals.

William Thomson (Lord Kelvin) derived (1.5) and (1.6) based on the use of classical thermodynamics of equilibrium reversible processes for isotropic medium, a more detailed study on the Thomson relations from thermodynamics of irreversible processes by Domenicali, and Samoilovich and Korenblit, shows that the expression of the Thomson relations does not change. The reason is that the Seebeck, Peltier, and Thomson effects in the isotropic medium can be regarded as "quasi-equilibrium" and "quasi-reversible" in the sense that their contribution to local entropy change ds/dt of unit volume is zero. For more information please refer to ref. [22].

#### 14. Summary

Based on the above introduction, this dissertation is the result of the research on the transport properties of thermoelectric materials, including the following questions. How do electrons and holes transport heat separately? How does the magnetic field affect the heat and charge conductions? How does the nanostructuring benefit the laminar TE materials? What are the thermoelectric transport properties of Pd doped UPt<sub>3</sub> single crystals?

Chapter 2 will describe the experimental equipment and techniques in our lab; Chapter 3 is devoted to the Lorenz number project for single crystal metals and semiconductors; Chapter 4 deals with the low temperature p-type laminar TE material Cu<sub>2</sub>Se with different dopants; Chapter 5 focuses on the electric conduction within thin bismuth films under applied magnetic field; Appendix B will talk about the experimental results of thermoelectric transport for Pd doped UPt<sub>3</sub> single crystals.

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# Chapter II: Experimental Techniques and Instruments

## 1. Introduction

In this Chapter, I will briefly introduce the experimental techniques used in our lab, as well as the ones used in this dissertation, and also the instruments in our lab that are equipped to achieve these synthesis and characterizations. As a measurement-oriented lab, we do not have enough experience in the synthesis. The instruments dedicated to fabrication are not as prevalent or professional as the ones for measurements. In the following part, the synthesis instruments and techniques are first introduced, and then followed with the measurement instruments and techniques. A flow of Cu<sub>2</sub>Se hot press (HP) nanocomposite fabrication process is presented in the end (it is also used to make MoSSe HP nanocomposite samples).

### 2. Single Zone Furnaces

There are two single zone furnaces in our lab, both of which were purchased from "MTI Corporation", as shown in Fig. 2.1. The left one is the horizontal ceramic tube

furnace EQ-GSL-1700X, which can safely reach a maximum temperature of 1500 °C, and the right one is the compact vertical quartz tube furnace OTF-1200X-S-VT, which can safely reach a maximum temperature of 1100 °C. Both of them can be used to grow certain simple crystal or realize some chemical reactions within a vacuumed ampoule; however, they have different optimized working temperature ranges, so the choice of furnace depends on the needed reaction temperature, as well as the gravity. Although it is not stated and suggested in the manual, sometimes we lay the vertical quartz tube furnace down, as shown in Fig. 2.20, to achieve a horizontal furnace in its optimized temperature range. The horizontal ceramic tube furnace should avoid this configuration, as it is impossible to hold it up as a vertical furnace, due to its structure.





Fig. 2.1: The left one is the horizontal furnace, with a higher maximum temperature limit. The right one is the vertical furnace, with a lower maximum temperature limit. They have different optimized working temperature ranges.

The left figure of Fig. 2.2 shows a vacuumed quartz ampoule, sitting in a horizontal alumina boat. The ampoule is vacuumed by a molecular pump to the order of  $10^{-6}$  mbar and then sealed by the H<sub>2</sub>/O<sub>2</sub> torch. The right figure of Fig. 2.2 shows three different enclosures and cases for the ampoule, which protect the furnaces tube from being cracked or damaged by the potential explosion of the ampoule during the chemical reactions. Besides synthesizing the desired materials, the furnaces were also used to anneal samples for better performance and quality.



Fig. 2.2: Quartz ampoule with raw Mo, S, and Se powder mixtures inside, and its three possible enclosures: rectangular alumina boat, stainless full safety enclosure, and graphite boat for ultra-high temperature usage.

# 3. Arc Melter

The left figure of Fig. 2.3 shows the arc melting machine "Arc Melt Furnace SA-200" from Materials Research Furnaces, Inc. It is used to synthesize some materials with high melting temperatures, which cannot be produced in our single zone furnaces. By applying the large current, the electric arc is able to heat the raw materials up to 3500 °C and produce enough thermal energy for the chemical reaction. The reactant is normally a first step "raw" material for the subsequent processes, such as the raw materials in the single zone furnace or in the ball milling jars. The right figure of Fig 2.3 shows the reactant from the arc melter, which is a mixture of iron and some other elements.



Fig. 2.3: Arc melter and the reactant. It is very important to turn on the water cooling of the arc melter.

# 4. Ball Mill

In addition to chemical reactions due to heat (*i.e.* thermal energy), the mechanical collision energy is also able to induce the reaction, especially if you want the reactant to be nanocomposites instead of single crystals. Meanwhile, the ball milling machine can also be used merely as a milling machine to crash large crystals into fine powders, of which the grain size is less than the order of microns. Fig. 2.4 shows the ball milling machine "8000D Dual Mixer/Mill" from SPEX SamplePrep LLC. When performing the ball milling processes, dual ball milling jars need to be placed in their positions to balance the cyclotron forces during the milling process. Different sizes of balls can be used in the ball milling jar. Fig. 2.4 shows several stainless steel balls of different sizes.



Fig. 2.4: 8000D Dual Mixer/Mill ball milling machine and two different ball milling jars. The left jar is homemade with an improved aspect when demounting the cap after the ball milling; the right one is a commercial jar, which may be difficult to open. A heavy metal brick is deployed on top of the ball milling machine to enhance the safety during the operation process.

# 5. X-ray Diffraction

X-ray diffraction (XRD), or called X-ray crystallography, is a characterization technique to identify the crystal structure of a material, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. Normally there are two types of XRD measurements: 1-D XRD curve and 2-D XRD pattern, both of which convert the 3-D lattice structure information into their own representations. The 1-D XRD curve is more commonly performed on powders, and from the diffraction angle  $2\theta$  of the diffraction peaks, as well as their intensity (less important than the  $2\theta$  angle), one is able to identify the composition(s) of the as-measured powders. The 2-D XRD pattern is more commonly performed on single crystals. It converts the 3-D information into 2-D diffraction patterns, where the symmetry tells the lattice structure and the luminance tells the different atom combinations. Fig. 2.5 shows a typical series of 1-D XRD curves of Cu<sub>2</sub>Se taken from this dissertation, which were performed on a Bruker D2 PHASER from Bruker Corporation.



Fig. 2.5: The desktop X-ray diffractometer Bruker D2 PHASER and the XRD curves of nanocomposite Cu<sub>2</sub>Se with different dopants measured on this machine.

# 6. Scanning Electron Microscopy (SEM)

Scanning electron microscopy is a type of electron microscopy, which explores the topography of a material by scanning a beam of focused electrons. Unlike the atomic-force microscopy (AFM), SEM demands the surface of the specimen be electron conducting. Thus, an insulated specimen needs to be sputtered with a fine layer of platinum or gold to ensure the conductance of the surface, while maintaining the topography. Fig. 2.6 shows the SEM used in our department "JEOL JSM-6340F Field Emission Scanning Electron Microscope" from JEOL USA, Inc. and a typical SEM image of the hot pressed (HP) nanocomposite Cu<sub>2</sub>Se parent compound taken from this dissertation, showing a typical grain size of several microns.



Fig. 2.6: A commercially available SEM device adjacent to Prof. Graph's lab and a typical SEM image of Cu<sub>2</sub>Se showing grain sizes on the order of several microns.

### 7. Physical Properties Measurement System (PPMS)

The "Physical Properties Measurement System", manufactured by Quantum Design, is the core equipment in Opeil's lab. Essentially, it is a refrigerator plus a magnet, which is able to provide a temperature range from 350 K to 2 K and a magnetic field from -9 T to +9 T. These two abilities provide us with the ability to perform all kinds of property measurements, such as electrical resistivity, Hall coefficient, thermal conductivity, Seebeck coefficient, specific heat, etc., through different commercially purchased options from Quantum Design. Besides, due to the functionality of a refrigerator and a magnet, more precise measurements can be performed with the help of other independent but more specific instruments, such as AC bridge (LR-700 from Linear Research Inc. or LS-370 from Lake Shore Cryotronics, Inc.) for resistance and Hall measurements, AH 2550A Capacitance/Loss Bridge from ANDEEN-HAGERLING, INC. for dilatometer and relative susceptibility measurements, SR830 Lock-In Amplifier from Stanford Research Systems for point-contact spectroscopy (PCS) measurements, etc. Fig. 2.7 shows the PPMS and its controllers Model 6000, 7100 and 6500. During daily use, sequence files are generated on the desktop PC and then sent into controllers through GPIB cables, the controllers then send commands in the sequence file to the PPMS to achieve certain measurements or establish certain circumstances, and return the signals back to the desktop and show them on the monitor. Sometimes an extra laptop is used to record data with the help of a LabVIEW program, because it cannot be executed simultaneously with the MultiVu program on the same PC.



Fig. 2.7: The Physical Properties Measurement System (PPMS) and its controllers Model 6000, 7100 and 6500. The blade hung by the pink wire is used to qualitatively detect the existence of the magnetic field. The right figure shows the operation of a dilatometer in the PPMS and the data was recorded by the laptop through a LabVIEW program.

The left figure of Fig. 2.8 shows the DC pucks and the AC pucks, which correspond to the resistivity option and AC transport option of PPMS, respectively. Both of them can be used to perform the electrical resistivity and Hall measurements. The right figure shows the sample holders used on the rotator probe, which are usually used for Hall coefficient measurements where the flip of the field is achieved through rotating the sample holder by 180 degrees, as well as used to measure the angle dependent field responds of all kinds of physical quantities, such as magnetoresistance, etc.



Fig. 2.8: DC pucks, AC pucks, and rotator sample holders, cigarette papers are used to electrically isolate the sample from the DC and AC pucks.

Fig. 2.9 shows the thermal transport option (TTO) puck and the heat capacity puck of PPMS. The TTO puck is used to measure thermal conductivity, Seebeck coefficient and electrical resistivity, while the heat capacity puck is used to perform the specific heat measurements. Because the air molecules will significantly affect the thermal transport at low temperatures, these two pucks need a high vacuum circumstance to operate properly.



Fig. 2.9: TTO puck and heat capacity puck. The left figure shows the chassis and the right figure shows the internal connections of these pucks.

As mentioned in the above paragraph, the PPMS can be used as a refrigerator and a magnet, to achieve the thermal expansion and differential resistance measurements, by using the dilatometer probe and the point contact spectroscopy probe, respectively. Fig. 2.10 shows the core part of these two probes. When performing the measurements, both probes are inserted into the "bottom" of PPMS chamber. A local thermometer (called "cernox") is placed below the sample holder at the bottom of the probes. With the help of the cernox a more precise temperature can be recorded during the experiments.



Fig. 2.10: The detailed portion of the dilatometer probe and the point contact spectroscopy (PCS) probe.

# 8. Sample Cutting

In order to mount any samples, they must be cut into the desired shape and dimensions that correspond to the configuration of the equipment. In our lab, samples are mainly cut by the diamond saws. Besides the diamond saws, the conducting materials can also be cut by the Electric Discharge Machine (EDM), where the sample is burned at the contact point. Fig. 2.11 shows the two different cutting systems. An aluminum rod is held in the brass parts of the EDM and is completely cut through by the copper wires. The right figure of Fig. 2.11 is a homemade diamond saw which is used to cut quartz tubes at a constant spin speed.



Fig. 2.11: The Electric Discharge Machining (EDM) system and a homemade diamond saw system. A 17-mm quartz tube is placed onto the diamond saw.

## 9. High Temperature Measurement Systems

The PPMS is used to perform low temperature measurements (usually below 300 K). The high temperature measurements are performed using two other systems: the homemade Kevin's setup and the commercial power conversion efficiency measuring instrument from ULVAC-RIKO, Inc.: Model ZEM-3, as shown in Fig. 2.12. The ZEM-3 is a commercial measurement system. However, the sample dimensions and shapes are restricted, and also the measured data points are limited (especially in the electrical resistivity measurements). As a result, the Kevin's setup was built by a former graduate student, Kevin Lucas, in Opeil's lab to overcome these limitations. Different from the ZEM-3, which is a complete measurement system and offers its own measurement ability, the Kevin's setup only supplies a high temperature and hermetically-sealed environment. All the measurements are achieved by the AC bridge (electrical resistivity) and Nanovoltmeter (Seebeck coefficient). Please refer to ref. [7,18] for more information on Kevin's setup.





Fig. 2.12: The ULVAC ZEM-3 and the Kevin's high temperature setup (refer to Kevin's dissertation ref. [18]) for high temperature electrical resistivity and Seebeck coefficient measurements.

### 10. Contact Connections: 4-Probe vs. 2-Probe

The definition of the electrical resistance is the ratio between the voltage V across the sample and the excitation current I through it along the same direction. So in daily life, the easiest way to know the resistance of a material is to use the multimeter to measure it. This is a standard 2-probe approach, and its principle is illustrated by the diagrams of Fig. 2.13. This method is pretty good if the contact resistance  $R_C$  is small compared with the resistance of the sample  $R_S$ . From the right diagram of Fig. 2.13 we can see that the real measured resistance also includes the contact resistance. If  $R_C$  is comparable with or even greater than  $R_S$  then the 2-probe method will give an incorrect result.



Fig. 2.13: The diagram and the principle of the 2-probe method to measure the electrical resistance by a multimeter.

The 4-probe method is introduced to overcome the contact resistance problem, as shown in Fig. 2.14. Although the contact resistance is still there and cannot be totally eliminated, with the 4-probe method, we are able to make use of the extremely high internal resistance characteristics of the voltmeter  $R_{\rm V}$ , which is usually on the order of M $\Omega$  (mega-ohm) or G $\Omega$  (giga-ohm) or even higher, and much greater than the resistance of the specimen  $R_{\rm S}$ . When we look at the right diagram of Fig. 2.14, we notice that the current going through the sample  $I_R$  is much greater than the one going through the voltmeter  $I_V$  (because  $R_V \gg R_S$ ), as a result  $I \approx I_R$ , meanwhile as long as the contact resistance  $R_{\rm C}$  is much less than the internal resistance of voltmeter  $R_{\rm V}$  ( $R_{\rm V} \gg R_{\rm C}$ ) then the reading of voltmeter is equal to the voltage across the sample, *i.e.*  $V \approx V_{\rm R}$ . Based on the above analysis the reading of the AC resistance bridge, which is always  $V/I \approx$  $V_{\rm R}/I_{\rm p} \equiv R_{\rm S}$ , the resistance of the sample. With the help of 4-probe method we are able to accurately measure the resistance of a specimen, as long as the contact resistance  $R_{\rm C}$  is much less than the one of the voltmeter  $R_V$  even if it is greater than the resistance of the sample  $R_{\rm S}$ . We relax the restriction from  $R_{\rm C} \ll R_{\rm S}$  in the 2-probe method to  $R_{\rm C} \ll$  $R_{\rm V} \sim M\Omega$  (at least) of the 4-probe method.



Fig. 2.14: The diagram and the principle of the 4-probe method, the resistance is usually measured by the AC bridge.



Fig. 2.15: The comparison between 2-probe and 4-probe method measurements. The left one shows the result between electrical resistivity of Cu<sub>2</sub>Se and the right one shows the result between thermal conductivity of FeSb<sub>2</sub> (from Mani's dissertation [1]).
Fig. 2.15 shows a comparison between 2-probe and 4-probe resistivity measurement of the same hot press (HP) nanocomposite Cu<sub>2</sub>Se parent compound, of which the electric contacts are made by silver epoxy. The plot explicitly shows the huge difference between the two methods, where the result from the 2-probe method is nearly 50 times more than the one from the 4-probe method, which means that the silver epoxy electric contacts themselves have large enough electrical resistance compared with and overwhelm the one of the Cu<sub>2</sub>Se specimen. As a result, the 2-probe method mainly gives the temperature dependent electrical resistivity of the silver epoxy rather than the sample we intend. However, from the 2-probe method we know that the resistance of the silver epoxy is much less than the internal resistance of the AC bridge. As a result, the readings from the 4-probe method are reliable and of course much less than the resistance of the silver epoxy, as shown in the left figure of Fig. 2.15.

The 4-probe technique may not have the same impact on the thermal conduction measurements. The right figure of Fig. 2.15 shows the comparison between thermal conductivity measurements of FeSb<sub>2</sub>, and we can see that the difference is negligible, as long as the contacts are made properly. The reason may be as follows: the thermal resistance of the contacts (usually the silver epoxy contacts) is small compared with the

thermal resistance of the sample. Unlike the case in the electrical conduction, the contacts do not play an important role in the thermal conduction and the 2-probe thermal conductivity measurements are normally acceptable (at least in our lab).

### 11. Thin Film Resistivity Measurement System (Van der Pauw Setup)

Normally, in order to measure the resistance of a specimen, its shape is important. It should be long and thin, so that when it is connected using a 4-probe method the current flows uniformly through the specimen. The left figure of Fig. 2.16 shows a standard 4-probe connection on a nanocomposite hot press Cu<sub>2</sub>Se sample mounted on a DC puck. The shape of the specimen is long and not wide. However, things cannot always be constructed as desired. The square shape samples are rare, especially in the thin film field, and as a result, a new technique is developed to measure the resistance of a two-dimensional (*i.e.* it is much thinner than it is wide), solid (no holes) material, and the electrodes are placed on its perimeter. This method was first propounded by Leo J. Van der Pauw in 1958 and as a result called the Van der Pauw method [2,3].

The principles and restrictions of the Van der Pauw method are discussed in detail in the literature [4,5]. In this section, I simply list several important formulae and

introduce the homemade Van der Pauw setup which is used to measure the electrical resistivity of thin films with constant thickness in our lab.



Fig. 2.16: The left figure shows a standard 4-probe connection from the DC puck channel 2 to the HP Cu<sub>2</sub>Se nanocomposite. Four copper wires are connected to the surface of Cu<sub>2</sub>Se by silver paint. The right figure shows the illustration of a square sample composed by four different resistors (1  $\Omega$ , 10  $\Omega$ , 100  $\Omega$  and 1000  $\Omega$ ) mounted on a DC puck (possibly the same one).

The Van der Pauw method is essentially a 4-probe method, and the four contacts are designated as 1, 2, 3, 4 in a counter clockwise order as shown in the right figure of Fig. 2.16. When using the AC bridge to perform the 4-probe measurements, one is able to have different resistance readings for different connection combinations. Let's define  $R_{ij,kl} \equiv V_{kl}/I_{ij}$ ,  $i \neq j \neq k \neq l$  as the reading of the AC bridge when voltage probes are connected to port k and l while current probes are connected to port i and j:

$$\begin{cases} R_{\rm v} = \frac{R_{12,43} + R_{34,21} + R_{21,34} + R_{43,12}}{4} \\ R_{\rm h} = \frac{R_{23,14} + R_{41,32} + R_{32,41} + R_{14,23}}{4} \end{cases}$$
(2.1)

where  $R_v$  and  $R_h$  represent the average resistance along the vertical and horizontal direction respectively. Then the sheet resistance  $R_s$  and resistivity  $\rho$  is calculated by the following formulae:

$$e^{-\pi R_{\rm v}/R_{\rm s}} + e^{-\pi R_{\rm h}/R_{\rm s}} = 1$$

$$\rho = R_{\rm s} \times t$$
(2.2)

(2.3)

where t is the thickness the thin film.

Because eight different configurations of  $R_{ij,kl}$  are needed for the Van der Pauw measurements, it is convenient to have an electric device to switch the configurations rather than manually do it, and a relay-switch is built for this aim. The left figure of Fig. 2.16 shows the physical product of this Van der Pauw setup. It includes the following parts:

- 1. DC puck: sample/thin film should be mounted in channel 2 and connected to the puck as shown in Fig. 2.16, the red cable of PPMS is needed.
- NI 9403/cDAQ-9171 chassis: used to transport the control signals from the laptop to the relay switch through USB port and 24-pin cable.
- Van der Pauw box: the electric switch controlling the connection of the sample. Its "vi" files have to be written by us because this hardware is homemade.
- 4. LR-700 AC bridge: used to measure the resistance in a 4-probe method.
- 5. The laptop: controls the configurations and records the results through LabVIEW program, which is not shown in Fig. 2.17.



4-resistor square



Fig. 2.17: Left figure shows the homemade Van der Pauw setup for thin film electrical resistivity measurements; right figure shows a preliminary Van der Pauw result of the 4-resistor in Fig. 2.16

A preliminary test of the 4-resistor in Fig. 2.16 is shown in the right figure of Fig. 2.17 from 250 K to 300 K, the result is not smooth and the program algorithm needs to be optimized. For more information on the Van der Pauw setup, please refer to the "Van der Pauw Manual" in our lab [6].

#### 12. Thin Film Thermal Conduction Measurement System ( $3\omega$ Setup)

As opposed to the electrical conduction, which is always conducted by the electrons (or holes equivalently, etc.) within the normal temperature range, heat transfer is categorized into three fundamental modes:

- 1. Conduction: the transfer of heat (internal energy) by microscopic collisions of particles and movement of electrons within a body. The physical quantity used to characterize this process is the thermal conductivity  $\kappa$ .  $\kappa$  can be measured by TTO of PPMS from low temperature to room temperature.
- Convection: the movement of groups of molecules within fluids such as liquids or gases, and within rheids. Now that our investigated thermoelectric materials are not fluids, thermal convection does not happen in the heat transfer.
- 3. Radiation: the emission or transmission of energy in the form of waves or particles

through space or through a material medium. In our thermoelectric area, it is limited to electromagnetic radiation, *i.e.* heat. The thermal radiation is negligible at low temperatures; however, it increases tremendously when temperature goes up. Above room temperature, it becomes as important as thermal conduction. One is not able to perform the thermal conductivity measurement using the same technique as in the TTO of PPMS, because the heat is not only conducted, but also radiated.

Due to the coexistence of both thermal conduction and thermal radiation, it is not possible to directly measure  $\kappa$  accurately above room temperature, *i.e.* both the commercial ZEM-3 and Kevin's setup cannot be used to perform the thermal conductivity measurement. As a result people have already developed an indirect approach, the laser flash analysis, to measure the thermal diffusivity of a bulk thermoelectric material and then derive the thermal conductivity. This method was first developed by Parker *et al.* in 1961 [9-11]. But the laser flash method is not suitable for a thin film measurement, because it also counts the contribution from the substrate of the film. The 3 $\omega$  method is an applicable technique used to measure the thermal conductivity of thin films, which was first proposed by David G. Cahill in 1990 [12-17]. Its principle is listed as following and in Fig. 2.18:

- 1. A gold or platinum heater is sputtered onto the surface of the thin film, where the thin film itself is deposited on a substrate. The heater is not only used to heat the film as a heat source, but also the resistance of the heater itself is monitored to reveal the instant temperature of the heater.
- 2. An AC excitation with circular frequency  $\omega$  is applied through the heater. The Joule heating changes with respect to time at a frequency of  $2\omega$  ( $P = I^2 R$ ), *i.e.* the Joule heating has components of  $0\omega$  (*i.e.* a constant) and  $2\omega$ .
- 3. Due to the Joule heating both the temperature and the resistance of the heater have components of  $0\omega$  and  $2\omega$ .
- 4. The AC voltage signal across the heater has components of  $1\omega$  and  $3\omega$  (V = IR). By measuring the  $3\omega$  component of the AC signal across the heater by the lock-in amplifier, one is able to extract the thermal conductivity of the thin film where the gold or platinum heater is sputtered. This is the reason why this method is called  $3\omega$ method, Fig. 2.18 shows how  $3\omega$  method works and Fig. 2.19 shows the real setup in our lab. For more detailed information on the homemade  $3\omega$  setup please refer to the " $3\omega$  Manual" in our lab [8].



Fig. 2.18: A schematic illustration of the 3ω principle, figure is taken from ref. [15]. Our setup is based on (a), (b) is a variant of the standard 3ω method that uses an AC+DC excitation.



Fig. 2.19: Schematic illustration of the experimental setup of a  $3\omega$  measurement and its realization – our homemade  $3\omega$  setup. The lock-in amplifier is used as the current source as well as the voltmeter.

# 13. Fabrication Processes of Hot Press Nanocomposites



Fig. 2.20: Schematic illustration of the fabrication processes of a hot press (HP) sample from the raw materials to the final HP ingot.

In this section I will briefly discuss the fabrication process of the as-fabricated hot press nanocomposite bulk samples in our lab, *e.g.* Cu<sub>2</sub>Se, MoSSe, etc., as shown in Fig. 2.20. The diagram illustrates the needed fundamental steps from the raw powders to the final hot press (HP) ingot:

- 1. Raw powders are mixed together in a glove box, where all chemicals are protected in an Ar atmosphere. The raw materials do not necessarily need to be fine powders, *i.e.* chunks or shots can also be used as raw materials for a chemical reaction. This depends on what kind of raw materials can we purchase. In this example of Cu<sub>2</sub>Se or MoSSe we start from powders. The mixtures are imported into an ampoule (*i.e.* quartz tube) in the glove box in an Ar atmosphere. After the ampoule is taken out of the glove box, it is pumped into a high vacuum with the help of a molecular pump and then sealed by a H<sub>2</sub>/O<sub>2</sub> torch. The pumping and sealing must be good enough to maintain a high vacuum and low pressure in the ampoule. Otherwise, the ampoule may explode when it is heated in the single zone furnace. As a result, when placing the ampoule into the stainless steel enclosure, shown in Fig. 2.2, it is a good idea to protect the tube of the furnace from being cracked.
- 2. The ampoule (with its enclosure) is placed into the furnace. The furnace is

programmed to heat and cool according to the chemical reaction conditions from literatures. In order to improve the quality of the reactant, the furnace is set to perform an annealing process at a temperature around 2/3 of the melting point of the reactant.

- 3. Crash the ampoule in the glove box and transfer the reactant into the ball milling jar in the Ar atmosphere. Dual ball milling jars are placed together into the ball milling machine to balance the cyclotron force. With appropriate ball milling time, we can get nanoscale fine powders. For our specimens, we only use the ball mill as a way to grind, however, because the mechanical collisions during the ball milling process are so strong and frequent that some raw materials are able to directly react in the ball milling jars, due to the mechanical energy, instead of the thermal energy in the furnace, and one is able to get the nanoscale fine powders from the raw reagents entirely in the ball milling process.
- 4. As mentioned previously the nanoscale grains are able to significantly scatter phonons and reduce the phonon thermal conduction. However, if the sample is not solid, its electrical conduction is also altered significantly. The hot press (HP) technique is a good approach to compress the powders into a solid ingot in a short period of time (less than two minutes) by applying a large current through the

powders under extremely high pressure. Due to the Joule heating, the small grains are able to grow and stick together and make the ingot solid. Besides, because the heating time is short, the grains do not have enough time to grow further and the merged ones are still on the order of sub-microns, *i.e.* through the HP process one is able to improve the electrical conduction of the ingot but maintain its poor phonon thermal conduction as intended.

5. Finally, we see the HP ingot as shown in the lower right corner of Fig. 2.20, and the thin disk-like specimens are cut by the diamond saw. Further cuts are needed to prepare a proper sample for electrical resistivity, thermal conductivity and Hall measurements.

#### References – Chapter II

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# Chapter III: Experimental Determination of Phonon Thermal Conductivity and Lorenz Ratio of Selected Single Crystals

## 1. Introduction

The thermal transport process is generally very complicated. However, for many materials at low temperatures, their thermal transport can be simplified into two categories, which are conducted by different carriers, namely [1,2]:

- 1) Electrical thermal conductivity  $\kappa_{e}$ , conducted by electrons or holes (fermions);
- 2) Phonon thermal conductivity  $\kappa_{ph}$ , conducted by phonons (bosons). This is equivalently called lattice thermal conductivity.

The total thermal conductivity is the sum of the above two components:  $\kappa_{tot} = \kappa_e + \kappa_{ph}$ . The contribution of  $\kappa_e$  or  $\kappa_{ph}$  to  $\kappa_{tot}$  is quite different for various single crystals and depends highly on their electrical properties. It can be roughly summarized as follows:

- 1) Metals:  $\kappa_{\rm e} \gg \kappa_{\rm ph}$ ;
- 2) Semimetals:  $\kappa_{\rm e} > \kappa_{\rm ph}$ ;

3) Semiconductors:  $\kappa_{\rm e} < \kappa_{\rm ph}$ ;

4) Insulators:  $\kappa_{\rm e} \ll \kappa_{\rm ph}$ .

If the material is not a single crystal, the defects and grain boundaries in the specimen will strongly affect the thermal transport of phonons and reduce  $\kappa_{ph}$  significantly [3-5]. However, it is not easy to model non-single crystals, such as nanocomposites, from first-principles calculation, so in this Chapter we only explore single crystal metals and semiconductors, which could afford first hand data for theoretical verification.

There's no doubt that  $\kappa_e$  and  $\kappa_{ph}$  are coupled together. In the literature, there are two main ways to separate them, both of which are based on the extrapolation:

 Dilute alloys. This method was mainly used to extrapolate phonon thermal conductivity in pure metals back to the environment of zero-impurity content of a series of dilute alloys in 1950s [2,6-8]. However, in practice it is a time-consuming and laborious approach because in order to apply this method, a series of good quality samples need to be prepared. Additionally, this method makes use of the Wiedemann-Franz law. As a result, the most reliable results are obtained at low temperatures, *e.g.* at a liquid helium temperature range [2]. 2) Magneto-thermo-resistance (MTR) [9,10]. By applying a sufficiently large transverse magnetic field to a specimen, the electronic transport is suppressed, which manifests in an increasing electrical resistivity  $\rho_{xx}$  and a decreasing electronic thermal conductivity  $\kappa_e$ . However, the phonon contribution  $\kappa_{ph}$  is not affected by the magnetic field by the assumption. When extrapolated to the limit  $\kappa_e \rightarrow 0$ , one is able to get the value of  $\kappa_{ph}$  and separate  $\kappa_{ph}$  from  $\kappa_{tot}$ .

Comparing the above two methods, the MTR method is obviously more economic. Additionally, modern labs are now able to supply a large enough magnetic field to accurately perform this measurement, with the help of the Physical Properties Measurement System (PPMS) from Quantum Design. Throughout this Chapter, the MTR method is adopted to separate and determine the value of  $\kappa_{ph}$ .

#### 2. Several Important Quantities and Formulae

When using the MTR method, one first needs to know what constitutes a strong magnetic field when applying it to a specimen. The deflecting angle  $\gamma$  of an electron away from its original linear motion under the influence of an applied magnetic field between two consecutive collisions is a parameter to identify the strength of the field

[11]:

$$\gamma \equiv \omega_{\rm c} \tau = \mu B = \frac{\sigma_0 B}{ne}$$
(3.1)

where  $\omega_c$  is the cyclotron frequency,  $\tau$  is the relaxation time,  $\mu$  is the mobility, B is the magnetic induction strength,  $\sigma_0$  is the electrical conductivity in zero field, n is the carrier concentration, and e is the elementary charge.

In practice, if  $\gamma = \mu B \sim 1$ , then the field is said to be strong [11] and a significant suppression of electronic transport should be expected. Here, for convenience, we can define a threshold field  $B_{th}$  as the inverse of mobility, *i.e.*  $B_{th} = 1/\mu$ , which is of course dependent on the material itself and also the temperature. If  $B_{th}$  at some temperature is smaller than the maximum field we can supply, then at that temperature we can see the suppression of total thermal conductivity  $\kappa_{tot}$  and an obvious magnetoresistance. For our sample, the suppression typically begins at 100 K and becomes significant below 60 K under our maximum applied 9 T field, which means  $\gamma$  becomes roughly greater than unity at this temperature range.

Zero-field Lorenz ratio is defined as

$$L \equiv \frac{\kappa_{\rm e}}{\sigma_0 T}$$
3-4

where  $\kappa_e$  is the electrical thermal conductivity,  $\sigma_0$  is the electrical conductivity, and *T* is the absolute temperature, with quantities representing values in the presence of zero field. The Lorenz ratio *L* is also an important quantity characterizing transport properties of electrons, and is widely used to estimate the electronic contribution  $\kappa_e$  to the total thermal conductivity  $\kappa_{tot}$  from the electrical resistivity  $\rho_{xx}$  measurements [12-15]. Its standard value, the Sommerfeld value,  $L_0 = \frac{\pi^2}{3} \left(\frac{k_B}{e}\right)^2 = 2.443 \times 10^{-8} \text{ V}^2/\text{K}^2$ , is derived from the validity of the Wiedemann-Franz law in metals and also by neglecting the thermoelectric term [1]. If the thermoelectric term cannot be omitted, the formula is modified as [1]:

$$L + S^2 = L_0$$
(3.3)

where *S* is the Seebeck coefficient. For metals, their Seebeck coefficients are normally on the order of several  $\mu$ V/K. As a result, the *S*<sup>2</sup> term can be neglected without any issue. However, for semiconductors, due to their large Seebeck coefficients, which are normally on the order of 100  $\mu$ V/K, *S*<sup>2</sup> is usually the same order of magnitude as *L*<sub>0</sub> and must be taken into account. When deriving the Sommerfeld value  $L_0$  there are two basic assumptions [2]:

- All scatterings are elastic, including the electron-phonon scatterings at high temperature and the impurity or defect scatterings at low temperature;
- 2) Both electrical and thermal transports have the same relaxation time.

For metals, these two assumptions are basically obeyed at low and high temperatures, and the Wiedemann-Franz law is established. However, in the intermediate temperature range, one or both of them are violated and the Lorenz ratio deviates from the Sommerfeld value  $L_0$ . By introducing different relaxation times for electrical and electronic thermal transports and discarding the electron-phonon Umklapp processes, the temperature dependence of dimensionless Lorenz ratio  $\tilde{L}$  of metals in zero field can be described as [2]:

$$\tilde{L} \equiv \frac{L}{L_0} = \frac{\kappa_0 - \kappa_{\rm ph}}{L_0 \sigma_0 T} = \frac{\beta + \left(\frac{T}{\Theta_{\rm D}}\right)^5 J_5 \left(\frac{\Theta_{\rm D}}{T}\right)}{\beta + \left(\frac{T}{\Theta_{\rm D}}\right)^5 J_5 \left(\frac{\Theta_{\rm D}}{T}\right) \left[1 + \frac{3\alpha^2}{\pi^2} \left(\frac{\Theta_{\rm D}}{T}\right)^2 - \frac{1}{2\pi^2} \frac{J_7(\Theta_{\rm D}/T)}{J_5(\Theta_{\rm D}/T)}\right]}$$
(3.4)

where  $\beta$  describes the purity of the sample,  $\alpha$  is the ratio between Fermi wave vector  $k_{\rm F}$  and Debye wave vector  $q_{\rm D}$ ,  $J_n$  is defined as:

$$J_n\left(\frac{\Theta}{T}\right) \equiv \int_{0}^{\Theta/T} \frac{x^n e^x}{(e^x - 1)^2} dx$$

and  $\Theta_D$  is the Debye temperature which can be estimated from the electrical resistivity through Bloch's  $T^5$  law [2,16]:

$$\rho(T) = \rho_{\rm imp} + \alpha_{\rm el-ph} \left(\frac{T}{\Theta_{\rm R}}\right)^5 J_5\left(\frac{\Theta_{\rm R}}{T}\right)$$
(3.6)

where  $\rho_{imp}$  is the residual resistivity,  $\alpha_{el-ph}$  the electron-phonon coupling constant and  $\Theta_R$  the resistivity Debye temperature. Although  $\Theta_D$  and  $\Theta_R$  are both called Debye temperatures,  $\Theta_D$  is more frequently extracted from the heat capacity measurements and its value is usually a little different from  $\Theta_R$ .



**FIGURE 2** Calculated  $(\kappa_e/\sigma T)/L_0$  versus  $T/\theta_D$  curves for various values of  $\rho_0/A$ , and for monovalent metals. The calculations are based on Eq. (33) using  $(k_F/q_D)^2 = \sqrt{[3]2/2}$  for monovalent metals.

Fig. 3.1: Simulation of eqn. (3.4) on different impurity levels, figure is taken from ref. [2]. Here  $\rho_0/A$  is  $\beta$  in eqn. (3.4) while  $k_F/q_D$  is  $\alpha$  in the formula.

Fig. 3.1 shows the simulation of eqn. (3.4) as a function of dimensionless temperature  $T/\Theta_D$ . The deviation from Wiedemann-Franz (W-F) law, *i.e.*  $\tilde{L}$  deviates from unity and is highly sensitive to impurities. If the sample is impurity free and absent any structural defects, only inelastic scattering effects are observed and the W-F law does not apply. This is observed in Fig. 3.1 where the solid curve goes to zero at  $\tilde{L}$  and  $T/\Theta_D$ . Elastic scattering arising from defects and impurities recovers the W-F law and this is illustrated in Fig. 3.1 by the broken lines which indicate various amounts of impurities and defects in the sample.

# 3. Electrical Conductivity $\sigma_{xx}$

The electrical resistivity and electrical conductivity are defined as the coefficients in the transport equations relating the current density  $\vec{j}$  with the electric field  $\vec{E}$ 

$$\vec{j} = \hat{\sigma}\vec{E}$$
 and  $\vec{E} = \hat{\rho}\vec{j}$ 
(3.7)

 $\hat{\sigma}$  is the inverse of  $\hat{\rho}$  and vice versa. In a uniform and isotropic material, both  $\hat{\sigma}$  and  $\hat{\rho}$  are reduced to scalars. However, in general cases, they are tensors and represented by 3×3

matrices, such as for single crystals and materials in a strong magnetic field.

If we choose the applied magnetic field direction as the z-axis, then the z-component of  $\hat{\sigma}$  or  $\hat{\rho}$  represent the longitudinal magnetoresistance as well as describe the coupling between longitudinal and transverse effects. As we know, since the transverse effect is normally much more prominent than the longitudinal effect and the coupling between them is not significant, the z-component can be neglected and both tensors reduce to 2×2 matrices [11]. For single crystals, the matrices can be further simplified if they satisfy the following requirements [11]:

- The single crystal is cubic and the magnetic field is along one of its high symmetry axis;
- 2) The single crystal is hexagonal and the magnetic field is along its c-axis.

(not due to the Onsager reciprocal relations) *i.e.* the applied magnetic field lies along an axis of sufficient symmetry [17]

$$\begin{cases} \rho_{xx} = \rho_{yy} \\ \rho_{xy} = -\rho_{yx} \end{cases} \text{ and } \begin{cases} \sigma_{xx} = \sigma_{yy} \\ \sigma_{xy} = -\sigma_{yx} \end{cases}$$
(3.8)

and the resistivity and conductivity tensors are represented as

$$\hat{\rho} = \begin{pmatrix} \rho_{xx} & -\rho_{yx} \\ \rho_{yx} & \rho_{xx} \end{pmatrix} \text{ and } \hat{\sigma} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ -\sigma_{xy} & \sigma_{xx} \end{pmatrix}$$

The electrical conductivity  $\sigma_{xx}$  can be derived from normal electrical resistivity  $\rho_{xx}$  and Hall resistivity  $\rho_{yx}$  measurements [11,17]

$$\sigma_{xx} = \frac{\rho_{xx}}{\rho_{xx}^2 + \rho_{yx}^2}$$
(3.10)

All of our samples satisfy the above requirements and these formulae can be applied.

With this being true, it is easy to find out that  $\sigma_{xx} \neq 1/\rho_{xx}$ , except in zero field, where  $\rho_{yx} = 0$ . Through the experiments, we use an AC bridge to measure electrical resistivity instead of directly gathering electrical conductivity data. From this choice, a natural question emerges: Does the resistivity data objectively represent  $\rho_{xx}$  or does it simply take the inverse of  $\sigma_{xx}$ , because the AC bridge only measures the voltage across the sample when applying a certain amount of excitation? The answer is that it depends on the experimental configuration. We know that in resistivity measurements, what we can control is the current, *i.e.* if we choose the current direction as x-axis then  $j_y = 0$ . If we explicitly write down (3.7) in our experimental environment

$$\begin{pmatrix} j_x \\ 0 \end{pmatrix} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ -\sigma_{xy} & \sigma_{xx} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} E_x \\ E_y \end{pmatrix} = \begin{pmatrix} \rho_{xx} & -\rho_{yx} \\ \rho_{yx} & \rho_{xx} \end{pmatrix} \begin{pmatrix} j_x \\ 0 \end{pmatrix}$$
(3.11)

As long as the AC bridge always outputs its data as the measured voltage divided by the excitation, then we can see clearly that the results are the resistivities  $\rho_{xx}$  and  $\rho_{yx}$  (precisely speaking the outputs are resistances rather than resistivities).

As a result, Hall measurements are important in order to get  $\sigma_{xx}$ . However, even with the help of the PPMS, it is still very challenging to perform Hall measurements on single crystal metals, due to their low resistivity and specimen dimension limit. As a result, the following formulae are used to aid in the extraction of  $\sigma_{xx}$  from magnetoresistance measurements: [11]

$$\frac{\rho_{xx}}{\rho_0} = \frac{\left[\frac{4c}{\pi}\left(1 - \frac{2\gamma}{\pi}\tanh\frac{\pi}{2\gamma}\right) + \frac{1}{1+\gamma^2}\right]\left(\frac{4c}{\pi} + 1\right)}{\left[\frac{4c}{\pi}\left(1 - \frac{2\gamma}{\pi}\tanh\frac{\pi}{2\gamma}\right) + \frac{1}{1+\gamma^2}\right]^2 + \left[\frac{8\gamma c}{\pi^2}\left(1 - \operatorname{sech}\frac{\pi}{2\gamma}\right) - \frac{\gamma}{1+\gamma^2}\right]^2}$$
(3.12)

$$\sigma_{xx} = \frac{\frac{4c}{\pi} \left( 1 - \frac{2\gamma}{\pi} \tanh \frac{\pi}{2\gamma} \right) + \frac{1}{1 + \gamma^2}}{\left(\frac{4c}{\pi} + 1\right) \rho_0}$$
(3.13)

where  $\rho_0$  is the zero field resistivity result,  $\gamma = \mu B$  is the deflecting angle, and *c* is another fitting parameter. For semiconductors there's no difficulty in performing the Hall measurements and (3.10) is applied, which is of course better than (3.13).

# 4. Extrapolation of Phonon Thermal Conductivity $\kappa_{ph}$

When extracting  $\kappa_{ph}$  from  $\kappa_{tot}$  it is important to know the functional form of both  $\kappa_{xx}(B)$  and  $\sigma_{xx}(B)$ , according to isotropic samples in the relaxation-time approximation [9,18] we have

$$\sigma(B) = \frac{\sigma_0}{1 + \mu_d^2 B^2}$$

$$\kappa_{\text{tot}}(B) = \kappa_{\text{ph}} + \frac{\kappa_0}{1 + \mu_t^2 B^2}$$
(3.14)

(3.15)

where  $\sigma_0$  and  $\kappa_0$  are the electrical and thermal conductivities in zero field,  $\mu_d$  and  $\mu_t$  are drift and thermal mobilities, respectively. Combine (3.14) and (3.15) together:

$$\kappa_{\text{tot}}(\sigma) = \kappa_{\text{ph}} + \frac{\kappa_0 - \kappa_{\text{ph}}}{1 + \lambda^2 \left(\frac{\sigma_0}{\sigma} - 1\right)}$$
(3.16)

where  $\lambda = \mu_t/\mu_d$  is considered as a fitting parameter. If  $\lambda$  equals unity,  $\kappa_{tot}$  and  $\sigma$  are linearly related, which happens at high temperature [9]. However, in general, it is not valid. The intercept of (3.16) is the phonon thermal conductivity  $\kappa_{ph}$ , where  $\sigma \rightarrow 0$  when the applied magnetic field is large enough. The accuracy of the extrapolation depends on how close the ( $\sigma(9T), \kappa_{tot}(9T)$ ) data point is to the intercept, having high

mobility in the sample and having sufficient suppression of electronic transport to assure the precision of this technique. Throughout the remainder of this Chapter,  $\kappa_{tot}$  and  $\kappa_{xx}$ are interchangeable with one another, because thermal conductivity measurements are normal measurements rather than Hall measurements and thermal conductivity is always measured including both components.

# 5. Experimental Details

As mentioned previously, in order to provide first hand data, which are more easily modeled through theoretical calculations, we choose single crystals as our specimen candidates to perform the measurements. The materials are chosen from two categories, either from commercial purchases or from Prof. Wilson's lab:

- 1) Single crystal metals:
  - Cu (100) 99.99% from MTI Co.;

Al (100) 99.999% from Goodfellow Cambridge Ltd.;

Zn (001) 99.999% from Goodfellow Cambridge Ltd.;

2) Single crystal semiconductors:

Bi<sub>2</sub>Te<sub>3</sub> from Prof. Wilson's lab;

Bi<sub>2</sub>Se<sub>3</sub> from Prof. Wilson's lab.

Basically, the experimental configurations are similar for both metals and semiconductors. They only differ slightly in final realizations. For metals, due to their extremely low resistivity, the contacts are soldered onto their surface. We first sputter metallic contacts on the surface of metals and then soldered the electrical contacts onto those metallic contacts in order to minimize the contact resistance. We use gold-coated copper sticks as the electrical contacts, which are also used in thermal transport measurements.

For semiconductors, because our samples are both bismuth compounds, use of silver is prohibited due to its diffusion into bismuth compounds. As a result, silver paint is not used directly on the surface of Bi<sub>2</sub>Te<sub>3</sub> or Bi<sub>2</sub>Se<sub>3</sub>. For resistivity measurements, we first put indium dots on the surface of the bismuth compounds and then press copper wires into the indium dots. After this, silver paint is used on the indium dots to create good electric contacts. Of course, we were very careful and made sure no silver paint dripped onto the sample. For thermal transport measurements, we built several brass clamps, which can hold the samples firmly by mechanical force. Gold-coated brass sticks are soldered onto these clamps. All contacts are connected in the standard 4-probe way.

Samples were cut into typical dimensions of  $1 \times 2 \times 10 \text{ mm}^3$  (metals) or  $1 \times 3.5 \times 10 \text{ mm}^3$  (semiconductors). Thermal conductivity and Seebeck coefficient measurements were performed using the thermal transport option (TTO) of the PPMS, in which the sample was placed in a transverse orientation, *i.e.* the magnetic field is perpendicular to the heat flow. When performing the experiments, we first fix the field and scan the temperature from 60 K to 5 K or in reverse, and then turn to another field. The field range is from 0 T to 9 T. A similar sequence is used for the electrical resistivity and Hall measurements by the LR-700 AC resistance bridge from Linear Research Inc., except we fix the temperature and scan the field. The sample is mounted in the same orientation as the one used for the thermal transport option.

#### 6. Magneto-Transport Measurements of Single Crystal Metals

Residual resistance ratio (RRR) defined by  $\rho_{300K}/\rho_{2K}$ , and resistivity Debye temperature  $\Theta_R$  fitted through (3.6) are summarized in Table 3.1. Our Debye temperature  $\Theta_D$  from the heat capacity measurements of the same samples confirms the consistency with  $\Theta_R$ .

Specimen	RRR	$\Theta_{ m R}/ m K$	$\Theta_{\rm D}/{\rm K}$	Field	Crystal
				Direction	Structure
Al (100)	200	415	395	(100)	fcc
Cu (100)	100	337	323	(100)	fcc
Zn (001)	800	221	233	(001)	hex

Table 3.1: Summary of magnetoresistance measurements

Fig. 3.2 shows the temperature behavior of total thermal conductivity and electrical resistivity. As mentioned above, the threshold field decreases when temperature goes down mainly due to the decrease of electrical resistivity. When applying the maximum field of 9 T, the suppression of electronic transport becomes significant below 60 K, which also means the threshold field roughly becomes smaller than the field we applied. The resistivity of Al and Cu shows the normal temperature behavior at low temperature, where both of them enter the residual resistance region, no matter what the applied field strength. However, the electrical resistivity of Zn in field is different from the ones of Al and Cu, which has a minimum outside of the residual resistance region. This "abnormality" is due to the fact that Zn is a compensated metal, which usually has a significant magnetoresistance phenomenon at low temperatures [11]. Additionally, as long as the thermal conductivity always approaches zero, there is a peak in the  $\kappa_{tot} \sim T$ curve, as shown in Fig. 3.2. However, the magnetic field broadens the peak, and also pushes the peak towards the high temperature direction when it is increased.



Fig. 3.2: Thermal conductivity and electrical resistivity vs. temperature between 5 K and 60 K (for Al and Cu) or 40 K (for Zn) in different magnetic fields. The insets illustrate the field effect on thermal conductivity for Al and Cu, electrical resistivity for Zn up to room temperature.


Fig. 3.2: Thermal conductivity and electrical resistivity vs. temperature between 5 K and 60 K (for Al and Cu) or 40 K (for Zn) in different magnetic fields. The insets illustrate the field effect on thermal conductivity for Al and Cu, electrical resistivity for Zn up to room temperature.



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Fig. 3.3: Total thermal conductivity is plotted against electrical conductivity at 5 K and 40 K. The top left inset in 5 K figure shows the magnetoresistance curve vs. the field along with its fit, while the bottom right inset shows the zoomed region at high fields. The two insets in 40 K figure show the field behavior of electrical and thermal conductivities along with their fits.



Fig. 3.3: Total thermal conductivity is plotted against electrical conductivity at 5 K and 40 K. The top left inset in 5 K figure shows the magnetoresistance curve vs. the field along with its fit, while the bottom right inset shows the zoomed region at high fields. The two insets in 40 K figure show the field behavior of electrical and thermal conductivities along with their fits.



Fig. 3.3: Total thermal conductivity is plotted against electrical conductivity at 5 K and 40 K. The top left inset in 5 K figure shows the magnetoresistance curve vs. the field along with its fit, while the bottom right inset shows the zoomed region at high fields. The two insets in 40 K figure show the field behavior of electrical and thermal conductivities along with their fits.



Fig. 3.4: Phonon thermal conductivity and dimensionless Lorenz ratio are plotted against temperature. The top figure also shows the total thermal conductivity in 9 T field, and the inset describes the contributions to the total thermal conductivity from phonons. The inset in the bottom figure illustrates the temperature behavior of the electronic thermal conductivity, compared with the total thermal conductivity, both in zero field.



Fig. 3.4: Phonon thermal conductivity and dimensionless Lorenz ratio are plotted against temperature. The top figure also shows the total thermal conductivity in 9 T field, and the inset describes the contributions to the total thermal conductivity from phonons. The inset in the bottom figure illustrates the temperature behavior of the electronic thermal conductivity, compared with the total thermal conductivity, both in zero field.



Fig. 3.4: Phonon thermal conductivity and dimensionless Lorenz ratio are plotted against temperature. The top figure also shows the total thermal conductivity in 9 T field, and the inset describes the contributions to the total thermal conductivity from phonons. The inset in the bottom figure illustrates the temperature behavior of the electronic thermal conductivity, compared with the total thermal conductivity, both in zero field.

In order to extract  $\kappa_{ph}$  from  $\kappa_{tot} \sim \sigma$  curves, the temperature needs to be held constant, Fig. 3.3 shows two of these extrapolations at 5 K and 40 K for each metal. All curves at 40 K have more linear behavior than at 5 K, because the electrical conductivity and electronic thermal conductivity have a more similar response to the field at higher temperatures [9]. The intercepts of these curves represent the value of  $\kappa_{ph}$ , which is assumed to be field independent. The top left insets in 5 K figures demonstrate the fit of magnetoresistance according to (3.12), and the top left insets in 40 K figures show the derived field dependence of electrical conductivity from the magnetoresistance fit based on (3.13), of course, at 40 K. The field dependence of total thermal conductivity is directly taken from the measurements, as described by the bottom right insets in 40 K figures. The bottom right insets in 5 K figures show a zoomed-in region of  $\kappa_{tot} \sim \sigma$ curves from 5 T to 9 T, and the extrapolations to the intercepts corresponding to the high field limit.

In top figure of Fig. 3.4, both  $\kappa_{ph}$  and  $\kappa_{tot}(9T)$  curves are plotted vs. temperature, as long as we assumed that  $\kappa_{ph} = \kappa_{tot}(\infty)$ . It is not surprising that  $\kappa_{ph}$ curve is below the  $\kappa_{tot}(9T)$  curve, and it should always be. The difference between the two curves is very tiny at the lowest temperature, which means the classically large magnetic field is reached. When temperature goes up, the 9 T field is not enough to suppress the electronic transport so the difference becomes larger. The insets in the top figure show the contribution from phonon to the total thermal transport. It is surprising that the ratio can go up to 50% for electron dominant metals (discussed further in the next section). However, the electronic and total thermal conductivity indeed have a similar temperature behavior as shown in the insets of the bottom figure. The dimensionless Lorenz ratio, shown in the bottom, deviates from unity when temperature goes up, where the transports are dominated by the electron-phonon scatterings. The results reveal that the relaxation time for thermal transport processes is shorter than the one for electrical processes [2], and are well described by (3.4).

From (3.4) we actually find out that the purity quantity  $\beta$  plays an important role in the Wiedemann-Franz law. If the sample is perfectly pure and without defect, then there is no impurity and defect scatterings with electrons at residual resistance temperature range. As a result, the Wiedemann-Franz law is violated and the Lorenz ratio approaches zero [2]. However, if there are impurities and defects, the Wiedemann-Franz law is recovered; as a result the  $\tilde{L} \sim T$  curve is concave and has a minimum at intermediate temperature range, see Fig. 3.1. Purer the sample, more concave the curve and smaller the minimum value of the Lorenz ratio [2]. If we examine the three  $\tilde{L} \sim T$  curves of Al, Cu and Zn, the Zn curve has the smallest Lorenz ratio at 40 K and also has the highest purity among them, which is indicated by the RRR values.

## 7. Discussions of the Results of Single Crystal Metals

The equations (3.4), (3.12), (3.14), (3.15) excellently describe the dimensionless Lorenz ratio, magnetoresistance, electrical conductivity and total thermal conductivity, respectively. However, when applying (3.16) to extract the phonon thermal conductivity  $\kappa_{ph}$ , care needs to be taken, especially when temperature goes up and the high field data points move away from the origin of  $\kappa_{tot} \sim \sigma$  plots. In such cases, the reliability of the extrapolation highly depends on the knowledge of the functional form of  $\kappa_{tot}(\sigma)$ . Thus  $\kappa_{ph}$  at higher temperatures, along with its ratio in the total thermal conductivity, need to be assigned with large uncertainties. As a result, the ratio may be overestimated.

Additionally, the ratio is also very sensitive to the purity of the specimen. The impurities and dislocations could significantly decrease the electronic transport, as is the situation in alloys, and increase the ratio of phonon contribution. The RRR values of our single crystal metals are on the order of 100, which is not high compared with the values

found in the literature, where its value can go beyond 1000 with a much larger experimental total thermal conductivity up to 10000 W/(m-K) [2,19-21]. Our Zn sample has the highest RRR value and its  $\kappa_{\rm ph}$  ratio is also the lowest at low temperatures.

The temperature behavior of  $\kappa_{\rm ph}$  depends upon the scattering mechanism. At low temperatures ( $T \ll \Theta_{\rm D}$ ), the phonons have a temperature dependence of  $T^3$  due to the specific heat and scatter with electrons having a temperature dependence of  $T^2$ respectively, while at high temperatures ( $T \gg \Theta_{\rm D}$ ) the Umklapp processes dominate the scattering with  $T^{-1}$  dependence. Thus, there is a peak in the  $\kappa_{\rm ph} \sim T$  curve, usually around 10% of the Debye temperature [1,2], as shown in Fig. 3.5.



Fig. 3.5: Phonon thermal conductivity of Al, Cu and Zn are plotted against temperature in a *log-log* scale. Two dashed lines are the guide lines of different temperature power laws.



Fig. 3.6: Electronic thermal conductivity of Al, Cu and Zn are plotted against temperature in a *log-log* scale at low temperature regime (5 K – 60 K) and total thermal conductivity at high temperature regime (100 K – 300 K). Two dashed lines in the left figure are the guide lines of different temperature power laws, while three dashed lines in the right figure are horizontal guide lines (*i.e.* constant,  $\sim T^0$ ) to the experimental data by averaging the data points from 200 K to 300 K.

Fig. 3.6 shows the temperature power law of  $\kappa_e$  at different temperature regimes. At low temperatures  $T^{-2}$  power law corresponds to the electron-electron scattering and  $T^{-1}$  power law corresponds to the residual resistance regime at even lower temperatures. We see  $\kappa_e$  of Al and Cu follow in between these two power laws, while the required low temperature for Zn is much lower than what we can supply. At the high temperature regime, our MTR method is not able to separate  $\kappa_e$  and  $\kappa_{ph}$  because of insufficient magnetic field. In the high temperature regime metals are electron dominant such that  $\kappa_e \approx \kappa_{tot}$ . The right figure in Fig. 3.6 shows the temperature dependence of  $\kappa_{tot}$  and we see that approaching to the room temperature all of three metals towards a constant thermal conductivity, which is a consequence of the large-angle elastic scatterings between electrons and phonons.

The requirement of high mobility is one of the requirements in this technique, which is needed to make the magnetic field achieved in the laboratory (~10 T) able to suppress the electronic transport. Also, the sample itself should not have bad electrical conduction. Otherwise, the relative change of electrical conduction is too small and all the points in the  $\kappa_{tot} \sim \sigma$  plot shrink together, which make the extrapolation to  $\sigma = 0$ unreliable. Due to the limitations of large magnetic field realized in the past and the materials themselves, very few single crystal metals were explored in transverse field, with the phonon thermal conductivity and the Lorenz ratio extracted. Some metals, such as Al [20], Cu [7,21-23], Zn [24], Au [20], Ag [20], have established results for the Lorenz ratio, found by using  $\kappa_{tot}$  instead of  $\kappa_e$ , since the function for estimating  $\kappa_e$  from  $\sigma$  was lacking, while  $\kappa_{ph}$  of Cu [6], Ni [8] were extracted with a different method. A benefit of measurements on single crystals is that it is possible to have a first-principles calculation on the field effect of these transport coefficients, which would be a very nice comparison between theory and experiment.

Further investigation would be to apply this method to semiconductor single crystals, such as Bi<sub>2</sub>Te<sub>3</sub>, Bi<sub>2</sub>Se<sub>3</sub>, etc., in which the phonon contribution is comparable with the electronic counterpart, or even dominant. As seen in metals, the Lorenz ratio drops quickly in the intermediate temperature range. If the Sommerfeld value is used to estimate  $\kappa_e$ , then the real electronic thermal conductivity is overestimated with huge errors. An improvement to the experiment for semiconductors is that it is much easier to make Hall measurement for semiconductor samples than for metal samples with similar dimensions. As a result, the electrical conductivity can be directly calculated from  $\rho_{xx}$ 

and  $\rho_{yx}$ , rather than from the fitting in (3.12). After the next section of supplementary materials of single crystal metals, we will continue discussing the experiments on semiconductors in this Chapter.

## 8. Supplementary Materials of Single Crystal Metals

In order to not interrupt the main stream of discussions on the results of single crystal metals, only select data were presented in the previous two sections. Here, in this supplementary section, I would like to provide more results on the magneto-transport measurements of single crystal metals, so that one can have a more comprehensive knowledge of the experiments and results.

Fig. 3S.1 shows the threshold field  $B_{\rm th} \equiv 1/\mu$  of our copper single crystal, where  $\mu$  is the mobility. If we compare  $1/\mu \sim T$  curve with  $\rho \sim T$  curve, we can find that they are actually very similar. The reason is because  $1/\mu = \rho ne$  where  $\rho$  is the electrical resistivity, n is the carrier concentration and e is the elementary charge. The carrier concentration n maintains the same order of magnitude throughout the whole temperature range. Thus, the electrical resistivity  $\rho$  mainly controls the temperature behavior of the threshold field. At room temperature, the threshold field is above 300 T, which by far exceeds the largest field we are able to supply. As a result, at room temperature range, we cannot observe the suppression as shown in Fig. 3.2. However, when the temperature goes down and enters the region where the threshold field is comparable to 10 T roughly, we should see a significantly suppressed  $\kappa_{tot}(9T)$  curve compared with the  $\kappa_{tot}(0T)$  one. Because Al and Zn are similar electron dominant metals to Cu, the shown threshold field analysis of Cu is also suitable for them, *i.e.* when the temperature is below 60 K, we should observe similar suppressions in both  $\kappa_{tot}$  and  $\sigma$  for Al and Zn.



Fig. 3S.1: The temperature dependent threshold field of Cu (100) single crystal. The right figure zooms in the low temperature part, when the temperature goes down to 40 K, the field needed is around 5 T, which is within our ability.

In order to apply the MTR method, we need to know the behavior of temperature dependence and field dependence of  $\kappa_{tot}$  and  $\rho$  simultaneously, *i.e.* we already map the measurements into 3-dimentional plots  $\kappa_{tot}(T,B)$  and  $\rho(T,B)$ , and also the derived  $\sigma(T, B)$ . We already know that all of the transport coefficients are tensors, so  $\sigma_{xx} \neq \sigma_{xx}$  $1/\rho_{xx}$ , but I still calculate  $1/\rho_{xx}$  and call it "pseudo electrical conductivity" and make a comparison in the following figures. Although  $\sigma_{xx} \neq 1/\rho_{xx}$  in general, we need to keep in mind that they are identical in zero field, *i.e.*  $\sigma_{xx}(0) = 1/\rho_{xx}(0)$ . So in the following  $\sigma_{xx} \sim T$  and  $1/\rho_{xx} \sim T$  plots, their uppermost curves (corresponding to zero field) are identical. Fig. 3S.2 contains the plots of Al, Fig. 3S.3 contains the plots for Cu and Fig. 3S.4 contains the plots for Zn. We can see that the electrical conductivity  $\sigma_{xx}$  is suppressed more than expected (estimation from  $1/\rho_{xx}$ ) at low temperatures due to the Hall effect. All of the following analyses are based on these data.

Fig. 3S.5, Fig. 3S.6 and Fig. 3S.7 show the direct extrapolations of  $\kappa_{ph}$  from  $\kappa_{tot} \sim \sigma$  curves for Al, Cu and Zn, respectively. The accuracy of extrapolation depends on how close the experimental data points are to the intercept. If we look at the extrapolations of Cu above 45 K, the results are not as good as the ones at lower temperatures and also the ones of Al and Zn at the same temperatures. The reason is

because Cu has a higher carrier concentration compared with the other two and as a result,

our applied field is unable to suppress the electrons enough.



Fig. 3S.2: Transport coefficients  $\kappa_{tot}$ ,  $\rho_{xx}$ ,  $\sigma_{xx}$  and  $1/\rho_{xx}$  of Al (100) single crystal. Supplement to Fig. 3.2. Note the difference between  $\sigma_{xx}$  and  $1/\rho_{xx}$  at high fields.



Fig. 3S.3: Transport coefficients  $\kappa_{tot}$ ,  $\rho_{xx}$ ,  $\sigma_{xx}$  and  $1/\rho_{xx}$  of Cu (100) single crystal. Supplement to Fig. 3.2. Note the difference between  $\sigma_{xx}$  and  $1/\rho_{xx}$  at high fields.



Fig. 3S.4: Transport coefficients  $\kappa_{tot}$ ,  $\rho_{xx}$ ,  $\sigma_{xx}$  and  $1/\rho_{xx}$  of Zn (001) single crystal. Supplement to Fig. 3.2. Note the difference between  $\sigma_{xx}$  and  $1/\rho_{xx}$  at high fields.



Fig. 3S.5: Extrapolations to extract  $\kappa_{ph}$  (the intercepts) from  $\kappa_{tot} \sim \sigma$  curves at twelve different temperatures of Al (100) single crystal. Supplement to Fig. 3.3.



Fig. 3S.5: Extrapolations to extract  $\kappa_{ph}$  (the intercepts) from  $\kappa_{tot} \sim \sigma$  curves at twelve different temperatures of Al (100) single crystal. Supplement to Fig. 3.3.



Fig. 3S.6: Extrapolations to extract  $\kappa_{ph}$  (the intercepts) from  $\kappa_{tot} \sim \sigma$  curves at ten different temperatures of Cu (100) single crystal. Supplement to Fig. 3.3.



Fig. 3S.6: Extrapolations to extract  $\kappa_{ph}$  (the intercepts) from  $\kappa_{tot} \sim \sigma$  curves at ten different temperatures of Cu (100) single crystal. Supplement to Fig. 3.3.



Fig. 3S.7: Extrapolations to extract  $\kappa_{ph}$  (the intercepts) from  $\kappa_{tot} \sim \sigma$  curves at eight different temperatures of Zn (001) single crystal. Supplement to Fig. 3.3.



Fig. 3S.7: Extrapolations to extract  $\kappa_{ph}$  (the intercepts) from  $\kappa_{tot} \sim \sigma$  curves at eight different temperatures of Zn (001) single crystal. Supplement to Fig. 3.3.



Fig. 3S.8: XRD patterns of Al (100), Cu (100), and Zn (001) single crystals, due to the systematic absence of the structural factor only (200), (200), and (002) peaks are observed.



Fig. 3S.8: XRD patterns of Al (100), Cu (100), and Zn (001) single crystals, due to the systematic absence of the structural factor only (200), (200), and (002) peaks are observed.

Fig. 3S.8 show the XRD patterns of our Al, Cu, and Zn specimen, and clearly demonstrate our samples are single crystals.

## 9. Magneto-Transport Measurements of Single Crystal Semiconductors

The magneto-transport measurements of semiconductors are quite different from metals in such a case that the suppression of  $\kappa_{tot}$  is not obvious throughout the whole temperature range. The reasons may be:

1) The specimen is phonon dominant. Even if the applied field is large enough and

greater than the threshold field, the suppression is not obvious because the portion of  $\kappa_e$  is tiny.

2) The threshold field is always greater than the maximum field we are able to apply and as a result, the suppression is not enough and  $\kappa_{tot}$  behaves inert to the field.

If it is the first situation, then ball milling the single crystal into nanocomposite is a very effective way to tremendously reduce  $\kappa_{ph}$ . With this method, the suppression is recovered in the nanocomposite [9].

Fig. 3.7 shows the threshold needed for Bi<sub>2</sub>Te<sub>3</sub> and Bi<sub>2</sub>Se<sub>3</sub> single crystals at low temperature. Clearly we see that Bi<sub>2</sub>Te<sub>3</sub> single crystal satisfies the criterion and is expected to have a much better result than Bi<sub>2</sub>Se<sub>3</sub> single crystal, whose threshold field is never reached, even at lowest temperatures we can get. As a result, in the following part within this section we only focus on the experiments and results of the Bi<sub>2</sub>Te<sub>3</sub> single crystal.



Fig. 3.7: The threshold field of Bi<sub>2</sub>Te<sub>3</sub> and Bi<sub>2</sub>Se<sub>3</sub> single crystals. Below 60 K the Bi<sub>2</sub>Te<sub>3</sub> will be fully suppressed under the maximum applied field of 9 T due to its low threshold field at this temperature range, while Bi<sub>2</sub>Se<sub>3</sub> will not be suppressed enough because its threshold field is always higher than what we can apply.

Fig. 3.8 shows the temperature behavior of total thermal conductivity and electrical resistivity. Due to the low carrier concentration of holes, distinct magnetoresistance is observed even at room temperature. However, on the contrary, the thermal conductivity is not suppressed much even when the threshold field is much lower than the magnetic field applied. The reason is because the thermal transport of Bi<sub>2</sub>Te<sub>3</sub> single crystal is phonon dominant. Compared with nanocomposites, the single crystals have much fewer impurities and defects.



Fig. 3.8: Total thermal conductivity  $\kappa_{tot}$  and electrical resistivity  $\rho$  are plotted against temperature between 5 K and 60 K in different magnetic fields. The inset illustrates the magnetoresistance up to room temperature, indicating that the criterion is already satisfied at room temperature.


Fig. 3.9: Total thermal conductivity  $\kappa_{xx}$  is plotted against electrical conductivity  $\sigma_{xx}$  at 10 K and 60 K respectively. The red fitted curve is calculated according to (3.16), the calculation of  $\sigma_{xx}$  is based on  $\rho_{xx}$  and  $\rho_{yx}$  according to (3.10), rather than from (3.12) and (3.13).



Fig. 3.10: Phonon thermal conductivity  $\kappa_{ph}$  and dimensionless Lorenz ratio  $\tilde{L}$  are plotted against temperature.  $1 - \frac{S^2}{L_0}$  is the modified Sommerfeld value according to (3.3), considering the thermoelectric term, *i.e.* the Seebeck effect. The inset in the top figure shows the proportion of phonon thermal conductivity to the total thermal conductivity, which always maintains a high value.

In order to extract  $\kappa_{ph}$  from  $\kappa_{tot} \sim \sigma$  curves, the temperature needs to be held constant. Fig. 3.9 shows two of these extrapolations at 10 K and 60 K. As shown in the literature [9]  $\kappa_{xx}$  and  $\sigma_{xx}$  become linearly related at high temperatures because the thermal mobility  $\mu_t$  and drift mobility  $\mu_d$  approach the same value. This is verified by the 60 K data. However, the situation at 10 K is very different. The intercept from the extrapolation corresponds to the pure phonon thermal conductivity  $\kappa_{ph}$ , and in this sense we separate the electronic and phonon thermal transport through the magnetic field.

In the top figure of Fig. 3.10 the phonon thermal conductivity  $\kappa_{ph}$  and total thermal conductivity at zero field  $\kappa_{tot}(0T)$  are plotted together. The upper right inset shows the proportion of phonon thermal conductivity to the total thermal conductivity. As we see for most of the temperatures, the ratio is above 90%, which also means the specimen is of good quality with few impurities and defects. The ratio only goes down at the lowest temperatures. This trend is also easily understood, since at low temperatures  $\kappa_{ph} \sim T^3$  while  $\kappa_e \sim T$ . As a result,  $\kappa_{ph}$  drops more quickly than  $\kappa_e$  in the low temperature range and its ratio to the total thermal conductivity decreases.

The dimensionless Lorenz ratio, defined as  $L/L_0$ , is shown in the bottom figure of Fig. 3.10. The dark cyan curve is the modified Sommerfeld value according to (3.3)

considering the thermoelectric effect, and the surrounding cyan spreading is its error bounds due to the uncertainty from the Seebeck coefficient measurements. The upper right inset shows the detailed comparison between 20 K and 60 K, and within this temperature range, the experiment and the theory corroborate with each other very well. The only inconsistency happens at 10 K, with its value going beyond unity tremendously (further discussion in the next section).

# 10. Discussions of the Results of Single Crystal Semiconductors

Eqns. (3.3) & (3.16) describe the dimensionless Lorenz ratio  $L/L_0$  and  $\kappa_{tot} \sim \sigma$  relationship very well. From Fig. 3.10 we see that except at 10 K, the Lorenz ratio is very close to its standard Sommerfeld value if the thermoelectric effect is considered, which means for Bi<sub>2</sub>Te<sub>3</sub> single crystal, the Wiedemann-Franz law is satisfied. At this temperature range, the relaxation time of the thermal process does not deviate from the one of electrical process. This may be due to the fact that our Bi<sub>2</sub>Te<sub>3</sub> only have RRR of 30 and are not pure enough, compared with the values of metal single crystals, which are one order of magnitude higher. In the literature, people have already reported that Bi<sub>2</sub>Te<sub>3</sub> single crystals might have a Lorenz ratio much larger than unity [25-27]. However, those

abnormalities are due to the bipolar contributions and the emerging temperature is quite different from and much higher than ours. We note that the carrier concentration (Fig. 3S.13) increases steadily with rising temperature suggesting that there is no bipolar contribution in our experimental regime (5 - 60 K). And we estimated the Fermi level to be 95 - 125 meV inside the valence band throughout the whole temperature range (5 - 125)300 K). One explanation of the huge Lorenz ratio at 10 K is the laminar structure of Bi<sub>2</sub>Te<sub>3</sub> single crystal. Normally due to the scattering, the mean free path of the electrons is smaller than the layer distance of Bi<sub>2</sub>Te<sub>3</sub> sheets. As a result, the specimen behaves as a 3-dimensional bulk material. However, as temperature going down, when the mean free path of electrons becomes greater than the layer distance, the electrons are restricted to the 2-dimensional structure and this transformation may result in a different Lorenz ratio from the Wiedemann-Franz law. Consistent with our results a notable violation of the Wiedemann-Franz law has been observed by Wakeham et al. [31] for Li<sub>0.9</sub>Mo<sub>6</sub>O<sub>17</sub> for T < 20 K in the one dimensional case. However, further experimentation is needed to confirm this.

When using (3.16) to extrapolate  $\kappa_{ph}$ , care needs to be taken. Fortunately, for our Bi<sub>2</sub>Te<sub>3</sub> samples, the threshold field is already achieved even at room temperature. As

a result, the 9 T data point is not far away from the intercept in both the 10 K figure and the 60 K figure. This situation guarantees the reliability of the extrapolation.

The temperature behavior of  $\kappa_{ph}$  depends on the scattering mechanism. In our Bi<sub>2</sub>Te<sub>3</sub> single crystals, the thermal transport is dominated by phonons, so we only need to consider the phonon-phonon scattering of the Umklapp process at high  $(T \gg \Theta_D)$  and intermediate ( $T \sim \Theta_D$ ) temperature ranges, with  $T^{-1}$  and  $e^{\Delta_{\min}/T}$  dependences respectively [1]. The phonon at low  $(T \ll \Theta_{\rm D})$  temperature range can be described with a  $T^3$  dependence due to its specific heat. As a result, there must be a peak in the  $\kappa_{\rm ph} \sim T$ curve. Fig. 3.11 shows the  $\kappa_{ph} \sim T$  curve in a log-log scale. At low temperatures, the curve deviates from the  $T^3$  power law. This is because 5 K is not low enough with respect to our Bi<sub>2</sub>Te<sub>3</sub> single crystal. If one has the data from 1 K, then the  $T^3$  law may be satisfied. After all, compared with our data of metals, the peak temperature of  $\kappa_{ph}$  of  $Bi_2Te_3$  is much lower. When the temperature goes higher,  $\kappa_{ph}$  begins to follow the  $e^{\Delta_{\min}/T}$  temperature dependence, as shown in the left figure of Fig. 3.11.



Fig. 3.11: Phonon thermal conductivity at low temperature and total thermal conductivity at high temperature of Bi<sub>2</sub>Te<sub>3</sub> single crystal is plotted against temperature in a *log-log* scale. Two dashed lines are the guide lines of different temperature dependences in both figures.

Right figure of Fig. 3.11 shows the temperature dependence of  $\kappa_{tot}$  at high temperature regime. We notice that  $\kappa_{tot}$  begins to tilt up above 250 K, and this is due to the contribution from bipolar effect  $\kappa_{bi}$ . Because at high temperature  $\kappa_e \sim \text{const}$ ,  $\kappa_{ph} \sim T^{-1}$ , and  $\kappa_{bi} \sim T$  (if other quantities are regarded constants, see eqn. (1.18)), as a result the power law dependence of  $\kappa_{tot} \sim T^{\alpha}$  should be between -1 and 0 ( $-1 < \alpha < 0$ ) when the bipolar contribution is small (100 K – 200 K), and we found that it is around -0.69.

The threshold field plays a key role in the MTR method. If it is not satisfied, *i.e.* the applied field is smaller than the threshold field, and then the suppression is not large enough. As a result, a specimen of high mobility is required. Usually this means that the RRR of the specimen cannot be small. Compared with the Bi<sub>2</sub>Te<sub>3</sub>, which has RRR of 30, we also perform the same experiments on Bi<sub>2</sub>Se<sub>3</sub> single crystals that have RRR of only 2. As a result, they have very low mobility, only one-tenth of the Bi<sub>2</sub>Te<sub>3</sub> value. Thus, the threshold field is never reached even at the lowest temperature we can provide. As a result, this Bi<sub>2</sub>Se<sub>3</sub> sample is not a good candidate to apply the MTR method.

Due to their larger resistance than metals, the Hall measurements are performed successfully on semiconductors and the electrical conductivity is calculated through (3.10). Although the electrical resistivity  $\rho_{xx}$  always increases when temperature goes up no matter the presence of magnetic fields, the electrical conductivity  $\sigma_{xx}$  does not always decrease. Starting from 3 T,  $\sigma_{xx}$  increases with temperature, which contradicts with our usual understanding. As a result, we will observe a crossover in the  $\sigma_{xx} \sim B$ curves in Fig. 3.12. This results from a large Hall resistance in our Bi<sub>2</sub>Te<sub>3</sub> sample and indicates that the cyclotron frequency,  $\omega_c$ , of the Landau levels due to the field becomes greater than the collision frequency  $1/\tau$  as the crossover emerges.



Fig. 3.12: Transverse electrical conductivity is plotted against magnetic field for different temperatures. A crossover is observed around 2.75 T.

### 11. Supplementary Materials of Single Crystal Semiconductors

Similar to the supplementary section on metals, in this part I would like to add some supplementary materials for Bi<sub>2</sub>Te<sub>3</sub> and Bi<sub>2</sub>Se<sub>3</sub> measurements.

For Bi<sub>2</sub>Te<sub>3</sub> single crystals, we are able to perform the Hall measurements. As a result, we have a chance to compare  $\sigma_{xx}$  among  $1/\rho_{xx}$ , Pippard's formula (3.13), or (3.10)  $\frac{\rho_{xx}}{\rho_{xx}^2 + \rho_{yx}^2}$  based on the symmetry of the specimen, as shown in Fig. 3S.9. Of course, all of these three formulae give the same result at zero field, but they deviate when the field begins to increase. At low temperatures, *e.g.* 5 K, the Pippard's formula is better than  $1/\rho_{xx}$ , and at high field limit it approaches the same result as (3.10). However, at high temperatures, none of them approaches the same result at a high field limit. Pippard's formula gives the worst results. In the temperature range of 5 K – 60 K that we focus on, Pippard's formula is better than  $1/\rho_{xx}$ , where the latter treats the transport coefficients as scalars. For metals, lacking the  $\rho_{yx}$  data, Pippard's formula is a reasonable way to extract the electrical conductivity  $\sigma_{xx}$ .



Fig. 3S.9: Comparison of the determination of  $\sigma_{xx}$  according to (3.10), (3.13) and  $1/\rho_{xx}$  at 5 K and 300 K.



Fig. 3S.10: Thermoelectric properties of Bi<sub>2</sub>Te<sub>3</sub> single crystal samples from 5 K to 300 K. The thermal transport option (TTO) of PPMS is set in the continuous measurements (default) mode.



Fig. 3S.10: Thermoelectric properties of Bi<sub>2</sub>Te<sub>3</sub> single crystal samples from 5 K to 300 K. The thermal transport option (TTO) of PPMS is set in the continuous measurements (default) mode.

From Fig. 3S.10 we can observe the field effect on Seebeck coefficient *S*, electrical resistivity  $\rho$  and the derived figure of merit *ZT*. However, the distinction in thermal conductivity  $\kappa$  is tiny, as mentioned in previous sections. One thing that needs to be noted is that because Bi<sub>2</sub>Te<sub>3</sub> is a phonon dominant thermal transport material, the default continuous measurements mode is not accurate enough to show the change. It even shows an opposite and wrong field effect on  $\kappa$  where  $\kappa_{tot}(9T) > \kappa_{tot}(0T)$  at low temperatures. This "abnormity" can be overcome by a more precise single steady-state measurements mode of TTO, and the  $\kappa_{tot}$  data in Fig. 3.8 are all gathered in this particular mode, where  $\kappa_{tot}(9T) < \kappa_{tot}(0T)$  correctly. The same situation happened for the Bi<sub>2</sub>Se<sub>3</sub> single crystal, as shown in Fig. 3S.11. Generally speaking, our Bi<sub>2</sub>Te<sub>3</sub> single crystal has better thermoelectric performance than the Bi<sub>2</sub>Se<sub>3</sub> single crystal.



Fig. 3S.11: Thermoelectric properties of Bi<sub>2</sub>Se<sub>3</sub> single crystal samples from 5 K to 300 K. The thermal transport option (TTO) of PPMS is set in the continuous measurements (default) mode.



Fig. 3S.11: Thermoelectric properties of Bi<sub>2</sub>Se<sub>3</sub> single crystal samples from 5 K to 300 K. The thermal transport option (TTO) of PPMS is set in the continuous measurements (default) mode.

Generally speaking, both Bi<sub>2</sub>Te<sub>3</sub> and Bi<sub>2</sub>Se<sub>3</sub> single crystals are good thermoelectric materials, but in practice the thermoelectric performance of materials themselves highly depends on the fabrication techniques, *i.e.* whether they are single crystals, polycrystallines, or nanocomposites [28-30]. Due to different quality of samples, our Bi<sub>2</sub>Te<sub>3</sub> sample has a roughly five times better thermoelectric performance (*i.e. ZT*, figure of merit) than Bi<sub>2</sub>Se<sub>3</sub>. But as long as both of them are single crystals, total thermal conductivity  $\kappa_{tot}$  is considerably large due to their high phonon conduction  $\kappa_{ph}$  and thus restricts the value of *ZT* if compared with nanocomposite bismuth compounds which usually double the value of *ZT* [28-30].

Fig. 3S.12 and Fig. 3S.13 show the direct extrapolations of  $\kappa_{ph}$  from  $\kappa_{tot} \sim \sigma$  curves for Bi<sub>2</sub>Te<sub>3</sub> and Bi<sub>2</sub>Se<sub>3</sub> single crystals respectively. The results of Bi<sub>2</sub>Te<sub>3</sub> are very similar to those of metals, as long as all of them approach high field circumstances. However, as shown in Fig. 3.7 Bi<sub>2</sub>Se<sub>3</sub> has never reached the threshold field. As a result, there are no data points appearing in the left half of six figures in Fig. 3S.13. Due to the fact that we do not know the exact functional form of  $\kappa_{tot}(\sigma)$ , if we still choose to apply (3.16) to extract  $\kappa_{ph}$ , the uncertainties become unacceptable.



Fig. 3S.12: Extrapolations to extract  $\kappa_{ph}$  (the intercepts) from  $\kappa_{tot} \sim \sigma$  curves at ten different temperatures of Bi<sub>2</sub>Te<sub>3</sub> (001) single crystal. Supplement to Fig. 3.9.



Fig. 3S.12: Extrapolations to extract  $\kappa_{ph}$  (the intercepts) from  $\kappa_{tot} \sim \sigma$  curves at ten different temperatures of Bi<sub>2</sub>Te<sub>3</sub> (001) single crystal. Supplement to Fig. 3.9.



Fig. 3S.13: Linear extrapolations to extract  $\kappa_{ph}$  (the intercepts) from  $\kappa_{tot} \sim \sigma$  curves at six different temperatures of Bi<sub>2</sub>Se<sub>3</sub> (001) single crystal, *i.e.*  $\lambda$  in eqn. (3.16) is set to unity manually.



Fig. 3S.14: XRD pattern and carrier concentration of our Bi<sub>2</sub>Te<sub>3</sub> single crystal sample.

Fig. 3S.14 demonstrate that our  $Bi_2Te_3$  sample is indeed a single crystal with a carrier concentration between 7 – 12  $10^{24}$  m<sup>-3</sup> throughout the whole temperature range, where it maintains nearly unchanged above 200 K.

# 12. Conclusions

The phonon thermal conductivity and Lorenz ratio of single crystal metals (Al, Cu and Zn) and single crystal Bi<sub>2</sub>Te<sub>3</sub> are extracted from the total thermal conductivity through the magnetothermal resistance measurements. The phonon thermal conductivity of metals typically has a peak around  $\Theta_D/10$ , while the Lorenz ratio of metals deviates from the Sommerfeld value in the intermediate temperature range but is well described by (3.4). The phonon thermal conductivity of Bi<sub>2</sub>Te<sub>3</sub> follows the expected temperature dependence in the intermediate temperature range. Except for the large value at 10 K, which may be due to the lower dimensional structures of Bi<sub>2</sub>Te<sub>3</sub>, the Lorenz ratio of Bi<sub>2</sub>Te<sub>3</sub> at other temperatures obeys the modified Wiedemann-Franz law (3.3) very well. Further investigation is required to compare the experimental results with the theoretical calculations from the first-principles. Now that the modeling for single crystals is much easier than for nanocomposites, the possibility of comparison between experiment and theory is exciting and expected. Our experimental data and analysis on Bi<sub>2</sub>Te<sub>3</sub> is an important compliment to previous measurements of Goldsmid [25] and theoretical calculations by Hellman *et al.* [32] at higher temperature 100 – 300 K.

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# Chapter IV: Low Temperature Thermoelectric Properties of *p*-type Copper Selenide with Different Dopants

# 1. Introduction

During the past several decades, physicists and engineers have devoted much effort to improving the conversion efficiency of thermoelectric (TE) materials, which are able to convert industrial waste heat into electricity. These solid-state materials have the potential to provide a renewable source of carbon free energy for our future [1,2]. The efficiency of the thermoelectric materials is characterized by the dimensionless quantity ZT called the figure of merit, defined by  $S^2T/\rho_{\kappa_{tot}}$ , where S, T,  $\rho$  and  $\kappa_{tot}$  are Seebeck coefficient, absolute temperature, electrical resistivity and total thermal conductivity, respectively. At low temperatures the total thermal conductivity  $\kappa_{tot}$  can be separated into two parts: the carrier (electrons, holes, etc.) part  $\kappa_e$  and phonon (or lattice) part  $\kappa_{ph}$ . Generally speaking, increasing the Seebeck coefficient and reducing the total thermal conductivity are the main methods to improve the value of figure of merit. In recent years reducing the phonon thermal conductivity  $\kappa_{ph}$  through the nanostructuring technique has proved to be the easiest and most straightforward approach [3-5]. The crucial point of the nanocomposite method is to introduce grain boundaries at the nanoscale whose sizes are larger than the mean free path of electrons but smaller than the one of phonons, as a result  $\kappa_{ph}$  would be significantly decreased while leaving other quantities unchanged or slightly altered. Besides employing a fabrication technique, the intrinsic properties of the material itself are also important in order to ensure a low thermal conductivity. For example, skutterudites and clathrates are shown to have complex structures with strong phonon scattering centers and have low thermal conductivity [6,7]; layered structure materials also are demonstrated to have high *ZT* values due to their high Seebeck coefficient and low thermal conductivity resulting from their low dimensionality [8-11].

Cu<sub>2</sub>Se is a layered compound which exhibits a second order structural phase transition at 130 °C from low temperature monoclinic  $\alpha$ -Cu<sub>2</sub>Se phase to high temperature anti-fluorite cubic  $\beta$ -Cu<sub>2</sub>Se phase [10,11], and is shown to have a peak in the temperature dependent *ZT* curve at this transition temperature and can be tuned by iodine doping [12]. Cu<sub>2</sub>Se has been extensively studied for its TE performance at temperatures above 300 K, which includes the phase transition at ~430 K. This higher temperature regime reflects the presence of a phonon-glass electron-crystal (PGEC), considered to be the origin of the high *ZT* value determined for this material [21-24]. A charge density wave (CDW) is a periodic modulation of the electronic charge density with an accompanying lattice structure distortion, which results from the formation of electron-hole pairs at the Fermi surface due to the instability of the lattice structure, and is usually induced by a perfect nesting on the Fermi surface [19].  $\alpha$ -Cu<sub>2</sub>Se is said to exhibit a CDW transition with Peierls distortion below 125 K according to its local maxima in the electrical resistivity measurements in that temperature regime [13-15], and may benefit its thermoelectric performance, where the enhancement from the Peierls distortion was reported in In<sub>4</sub>Se<sub>3- $\delta$ </sub> crystals from CDW state [8]. Inspired by the above facts,  $\alpha$ -Cu<sub>2</sub>Se could very likely have a low thermal conductivity and a high figure of merit, and could be also tuned by different dopants.

In the situation of singlet superconductors where the BCS theory is applied, the electron pair consists of two electrons with opposite spins and results in a Cooper pair with zero total spin, zero total momentum and breaks the gauge symmetry. The electron-hole pair emergent in CDW consists of one electron and one hole with the same spin and results in a pair with zero total spin but a nonzero total momentum, and thus breaks the translational symmetry. The pair formation is very similar to the Cooper pair

formation in superconductors, as a result the BCS description and estimation are suitable here [19,26,27]. The appearance of CDW is considered as a continuous transition, *i.e.* the Peierls transition, due to the re-arrangement of electronic wave functions driven by the strong phonon-electron interactions at low temperature. The CDW is usually observed in single crystalline materials with layered or chain sub-crystalline structures, such as NbSe<sub>3</sub> [16,28,29], TaS<sub>3</sub> [17], K<sub>0,3</sub>MoO<sub>3</sub> [30], (TaSe<sub>4</sub>)<sub>2</sub>I [18], KNi<sub>2</sub>S<sub>2</sub> [31] and La<sub>1,9</sub>Sr<sub>0,1</sub>CuO<sub>4</sub> [32]. Due to the appearance of CDW, abnormal temperature dependent electrical resistivity and also nonlinear I-V curve beyond the threshold electric field were observed [16-18,28-30]. Additionally, the coupling effect between electron and phonon was also confirmed by the magnetic susceptibility [33] and heat capacity measurements [34]. However, the ground state with charge density wave is quite weak, which could be broken or depinned by an electric field [17,18,28-30], a magnetic field [35], or pressure [16]. The CDW transition is, therefore, experimentally observed only in high purity thin single crystalline samples such as films or whiskers.

The CDW transition could be smeared out as the materials going from 2D-film to 3D-bulk [19], and also as the materials going from single crystals to polycrystals [36]. In this Chapter, we reported a new CDW ground state which was observed in Cu<sub>2</sub>Se in a polycrystalline bulk near 125 K. The coupling strength was interpreted by the amplification of the resistivity hump near the transition temperature. The Hall effect measurements suggest the Peierls transition starting near 160 K and ending near 90 K. After  $Cu_2Se$  enters a new CDW ground state, a negative differential resistivity is observed in the *dc* I-V curve below the critical electric field near 50 K for the first time.

It is important to clarify that the method to confirm the presence of a CDW phenomenon results from, *e.g.* STM scanning, where the modulation of charge density in space can be revealed directly and this periodic modulation is called charge density wave. I have found no literature reports of STM measurements on single crystal  $\alpha$ -Cu<sub>2</sub>Se to confirm the presence of a CDW wave at low temperature (~125 K), however, there are several electrical measurements on polycrystalline samples and all of them indicate a "hump" in the  $\rho \sim T$  curves in the low temperature regime. These papers assert that the abnormality in electrical resistivity arises from an underlying CDW [13-15]. Throughout this Chapter I adopt the assertion of the previous authors that it is not an unreasonable assumption that a CDW arises in  $\alpha$ -Cu<sub>2</sub>Se in the low temperature regime. The reasons for accepting this assertion are explained in detail in the following sections:

1. Non-linear electrical resistivity measurement, the "hump" or the sharper "peak" is an

indication of CDW.

- 2. The increase of electrical resistivity is due to the (partial) disappearance of Fermi surface.
- Because of the reduced Fermi surface, the carrier concentration should decrease and mobility should change within the transition regime, and these are all confirmed by our measurements and calculations.
- 4. Isoelectronic element replacing (*e.g.* Te and Ag doping) will change the band structure and break the perfect nesting on the Fermi surface, and kill the CDW transition.

All of the above statements are self-consistent, and by using the concept of CDW we are able to explain most of our result, so that's the reason I use CDW here. In the following descriptions in this Chapter, whether indicated explicitly or not, the CDW in our  $\alpha$ -Cu<sub>2</sub>Se samples is presumed which is undemonstrated directly from STM.

Also, besides the above effects, there is a phenomenon called a sliding CDW. When a CDW is formed during the transition, it is frozen within the lattice and cannot move within the sample, in other words it is pinned in the lattice. However, it can be depinned if a large enough electric field is applied, and meanwhile the sample shows a decrease in its electrical resistance. A deflection was observed in the 4-probe dc I-V curve measurement as described by G. Grüner when the current is higher than a threshold value corresponding to the threshold electric field [19]. This is the motivation behind undertaking dc I-V curve measurements for our samples. However, our samples do not have a large enough resistance (current is limited in the experiments), therefore the threshold field is never reached and no sudden change of slope is observed in the I-V curve.

# 2. Experimental Details

The bulk nanocomposite  $\alpha$ -Cu<sub>2</sub>Se samples with different dopants (2% Zn, 10% Ni, 10% Te, 10% Ag) were synthesized by mechanical ball milling (BM) and hot pressing (HP) at 700 °C. This synthesis technique is similar to our previous work on Cu<sub>2</sub>Se at T > 300 K [11,13]. The typical grain size of the as-fabricated sample is on the order of  $1 - 2 \mu$ m, and the samples have typical dimensions of  $1 \times 3 \times 10$  mm. An LR-700 AC resistivity bridge from Linear Research Inc. was used to perform the electrical resistivity and Hall coefficient measurements from 5 to 300 K using a standard 4-probe method. The thermal conductivity and Seebeck coefficient were measured by the thermal transport

option (TTO) from Quantum Design – PPMS with a 2-probe method. The *dc* I-V curve of the sample is measured by the standard 4-probe method with Keithley 224 current source, and Agilent 34410A  $6\frac{1}{2}$  Digit multimeter or Keithley 2182A nanovoltmeter. In all temperature dependent experiments the temperature is controlled and monitored by a Quantum Design PPMS with a sweeping speed of 0.5 K/min. The errors for the measurements were calculated from the standard deviation and propagation of errors, and were determined to be 4% for thermal conductivity, 5% for Seebeck coefficient, and 11% for figure of merit *ZT*.

### 3. Structure and Transport Measurements

As mentioned previously Cu<sub>2</sub>Se is a *p*-type semiconductor and has a structural transition at around 130 °C, and the low temperature phase and high temperature phase are designated as  $\alpha$ -phase ( $\alpha$ -Cu<sub>2</sub>Se) and  $\beta$ -phase ( $\beta$ -Cu<sub>2</sub>Se) respectively. Similarly Ag<sub>2</sub>Se also performs a structural transition at a near temperature; however, in literatures people prefer to designate the low temperature phase as  $\beta$ -phase and the high temperature phase as  $\alpha$ -phase, which is just opposite to the convention used for Cu<sub>2</sub>Se [44-46]. Furthermore, CuAgSe follows the same convention as Ag<sub>2</sub>Se [44-46]. Different from Cu<sub>2</sub>Se, Ag<sub>2</sub>Se is

*n*-type, as a result the Ag doping is not a good approach to improve the TE efficiency of  $Cu_2Se$ . Meanwhile CuAgSe is also an *n*-type material; it looks like Ag produces more charge of carriers than Cu in the compound but with an opposite sign. Because there's no benefit from the Ag doping, the results of  $Cu_{1.9}Ag_{0.1}Se$  are organized as an individual section aside from others in this Chapter.

Fig. 4.1(a) shows the powders XRD pattern of the polycrystalline Cu<sub>2</sub>Se made by ball milling and hot pressing. The XRD measurement was conducted on a Brucker D2 PHASER system at room temperature with a scanning speed of 10 seconds per/step (step size =  $0.014^{\circ}$ ). Rietveld refinement was done in Fullprof suite by using monoclinic structure (space group C2/c, No. 15) as the starting structure, which was recently proposed by Gulay [37]. The monoclinic  $\alpha$ -Cu<sub>2</sub>Se shows a lamella sub-lattice structure along ab-plane, which is similar to its high temperature cubic  $\beta$ -Cu<sub>2</sub>Se [11]. The interesting feature of each lamella is the hexagonal-ring chain made by Cu<sub>3</sub>Se<sub>3</sub>, which is outlined in stick mode crystalline structure, as shown in the Fig. 4.1(b). However, the direction of connected Cu<sub>3</sub>Se<sub>3</sub> chain between two lamellas is different. The one-dimensional hexagonal ring chain could generate the electronic density instability associated with the electron-phonon coupling effect. Research on the crystal structure of Cu<sub>2</sub>Se has shown that several crystallographic structures may be present depending on the temperature [25]. Our XRD refinement calculation shows a monoclinic structure of Cu<sub>2</sub>Se [13].

Fig. 4.1(c) shows the temperature dependent electrical resistivity of a typical polycrystalline Cu<sub>2</sub>Se. Reversible non-linear temperature dependent electrical transport properties are observed for the entire "cool down + warm up" temperature cycle. Below room temperature, the resistivity initially shows the behavior of a diffusion-controlling metal-like behavior, corresponding to a nearly unchanged carrier concentration and increasing carrier mobility with temperature as shown in Fig. 4.3. The electrical resistivity starts to deviate from such behavior when the temperature goes down to near 160 K and forms a "hump" in temperature range from 160 K down to 80 K. The similar abnormity in dc electrical resistivity was characterized as the appearance of CDW in NbSe<sub>3</sub>, TaS<sub>3</sub> and K<sub>0.3</sub>MoO<sub>3</sub> [16-18,28-30]. Additionally, a hysteresis loop in the temperature dependent electrical resistivity was observed in the range of 80 – 160 K. Conventionally, the sharp peak in the curve of logarithmic derivative of electrical resistivity  $(\ln \rho, \text{ or } \log \rho)$  with respect to reciprocal temperature 1/T, *i.e.*,  $d\{\log \rho(T)\}/d(1/T)$  versus T, was used to define the character temperature of the Peierls transition. By applying the same method, we determined the transition temperature  $T_{\rm C}$  is 125 K, as shown in the Fig. 4.1(d). Due to the polycrystalline structure, the Peierls transition process has a widely expanded temperature range from 160 K to 90

K.


Fig. 4.1: (a) Powder XRD pattern of as-fabricated polycrystalline Cu<sub>2</sub>Se at room temperature, in which the calculated pattern is based on a monoclinic structure C2/c (No. 15). The refine

structure ( $R_p = 2.48$  %,  $R_w = 3.33$  %,  $R_{exp} = 0.44$  %) shows the Cu<sub>2</sub>Se has a monoclinic unit cell (a = 7.1310 Å, b = 12.3517 Å, c = 27.2880 Å,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 94.39^\circ$ ). (b) The atomic structure of monoclinic Cu<sub>2</sub>Se in stick mode with hexagonal-ring chain is shown with the atoms, in which the green ones are Se atoms, and the blue ones are Cu atoms. (c) Temperature dependent electrical resistivity is measured in both the cooling and heating processes. (d) Temperature dependence of d{log  $\rho(T)$ }/d(1/T) . The inset is the varying Hall carrier concentration in the Peierls transition process. (e) Saturated energy gap due to CDW at 0 K as a function of the transition temperature for Cu<sub>2</sub>Se and other CDW materials. (f) Electron-phonon coupling constant as a function of the transition temperature for Cu<sub>2</sub>Se and electron-phonon coupling constants of NbSe<sub>3</sub>, TaS<sub>3</sub>, K<sub>0.03</sub>MoO<sub>3</sub>, KCP, (TaS<sub>4</sub>)<sub>2</sub>I were adapted from ref. [19].

According to the mean field theory [19], the elevated electrical resistivity with decreasing temperature, follows the activation energy relationship, *i.e.*,  $\rho \propto \exp(\Delta/k_{\rm B}T)$ where the  $\Delta$  is the effective energy gap due to the CDW. The energy gap could be obtained by extracting the slope of the curve of  $\log \rho$  vs. 1/T. Fig. 4.1(e) shows the numerical calculation of the  $\Delta$  by using a differential step value  $\delta T = 1$  K, and shows a temperature dependent energy gap of  $\Delta = 40.9 - 0.265 T$  (meV). We note that the exact physical meaning of the temperature dependent  $\Delta(T)$  is not clear. It could be an average result of all the grains or domains with and without an open gap. The saturated energy gap at zero temperature is estimated to be 40.9 meV by applying the  $T \rightarrow 0$  according to the linear relationship. Fig. 4.1(e) compares the saturated energy gap of Cu<sub>2</sub>Se with other reported CDW materials as a function of their Peierls transition temperature. The value of  $\frac{\Delta}{k_{\rm B}T_{\rm C}}$  for all the samples is larger than the theoretical Bardeen-Cooper-Schrieffer (BCS) relationship, *i.e.*,  $2\Delta = 3.52 k_B T_{CDW}^{MF}$ , which means that the real observed Peierls transition temperature is much lower than the theoretical value based on the mean field theory. Furthermore, the electron-phonon coupling constant  $\lambda$  and the coherent length of electron-hole pair  $\xi_0$  of the CDW ground state could be estimated within the free electron model by using the following relationships [19],

$$\Delta = 2\epsilon_{\rm F} {\rm e}^{-1/\lambda}$$
4-14

(4.1)

$$\xi_0 = \frac{\hbar v_F}{\pi |\Delta|}$$

$$\epsilon_F = \frac{\hbar^2}{2m_0} (3\pi^2 n)^{2/3}$$

$$(4.2)$$

$$(4.3)$$

$$v_{\rm F} = \left(\frac{2\epsilon_{\rm F}}{m_0}\right)^{1/2} \tag{4.4}$$

where  $\hbar$  is the reduced Planck constant,  $m_0$  is the free electron mass, and n is the carrier concentration at zero temperature. By using the carrier concentration near 90 K, *i.e.*,  $n = 1.6 \times 10^{20}$  cm<sup>-3</sup>, to Eq. (4.1 – 4.4), we derive the characterized parameters:  $\epsilon_F = 0.11 \text{ eV}$ ,  $v_F = 1.94 \times 10^7$  cm s<sup>-1</sup>,  $\lambda = 0.6$ , and  $\xi_0 = 1 \text{ nm}$ . Fig. 4.1(f) shows the coupling constant  $\lambda$  vs. transition temperature of several single crystal compounds from literature, *e.g.* NbSe<sub>3</sub>, TaS<sub>3</sub>, K<sub>0.3</sub>MoO<sub>3</sub>, KCP, and (TaSe<sub>4</sub>)<sub>2</sub>I, as well as, our polycrystalline Cu<sub>2</sub>Se. The coherent length of electron-hole pair  $\xi_0$  of Cu<sub>2</sub>Se is one order of magnitude less than K<sub>0.3</sub>MoO<sub>3</sub> and (TaSe<sub>4</sub>)<sub>2</sub>I, and also 6 times less than NbSe<sub>3</sub>. The  $\xi_0$  of as-fabricated Cu<sub>2</sub>Se is much smaller than the grain size of 1 µm, which could explain why we are able to observe the CDW in poly-crystalline Cu<sub>2</sub>Se. We also show the direct measurement of a cold pressed sample from the Cu<sub>2</sub>Se nano-powder. It is found that

non-linear electrical resistivity due to CDW is significantly suppressed. A restored CDW ground state was seen by annealing the cold pressed sample, which demonstrates the behavior of the cold pressed sample as the nano-grains merged into micro-grains. The restoration of the "hump" in electrical resistivity is shown in Fig. 4.2. From Fig. 4.5 we can see that the cold press sample has a much small grain size than hot press or cold press + anneal samples, thus it has more scatterings during the charge transport and this results in a larger electrical resistivity across the (nearly) whole temperature range we studied.



Fig. 4.2: The annealed cold press Cu<sub>2</sub>Se sample shows a partial restoration of nonlinear electrical resistivity. The amplitude and the range of the "hump" of the annealed cold press sample are both reduced compared with the hot press sample, but the transition temperature derived from  $d\{\log \rho(T)\}/d(1/T)$  is close.



Fig. 4.3: Temperature dependent Hall carrier concentration (a) and mobility (b), a standard 4-probe Hall resistance method was performed; measurements were carried out in both +6 T and -6 T magnetic fields, in order to eliminate the asymmetric effect from the 2 voltage leads. (c - g) I-V curves at different temperatures, in which the regular oscillations only appear at 50 K.

Fig. 4.3 shows a greater detail of Hall measurements of Cu<sub>2</sub>Se, which demonstrates several complicated features near the Peierls transition. The Hall carrier concentration of  $Cu_2Se$ , as shown in Fig. 4.3(a), is almost a constant as the temperature decreases from room temperature to 160 K, and then gradually decreases from  $2.1 \times 10^{20}$ cm<sup>-3</sup> to  $1.6 \times 10^{20}$  cm<sup>-3</sup> as the temperature goes down further from 160 K to around 90 K. and finally reaches a stable value below 90 K. The decreasing carrier concentration from 160 K to 90 K was interpreted as the appearance of the charge density wave, which corresponds to the formation of electron-hole pairs in real space and a decrease of the area of the Fermi surface in reciprocal space. In addition, in Fig. 4.3(b), the carrier mobility also shows three stages in the temperature dependent curve, which is consistent with the variation of the carrier concentration. Near room temperature, the temperature dependent carrier mobility shows a typical degenerated semiconductor behavior with acoustic phonon scattering, *i.e.*, r = 0.8 - 1.2 in the relationship of  $\mu \propto T^{-r}$  at this temperature range. The power index shows a continuous decrease to almost zero when temperature goes from 300 K to 160 K, which may be due to the onset of the CDW. During the phase transition temperature range from 160 K to 90 K, carrier mobility is nearly flat. After entering the CDW ground state, the carrier mobility starts to rise again in a more gentle way. The electrical resistivity does not follow the relationship as

expected for a normal metal. The temperature dependent carrier concentration and carrier mobility divide the temperature range into three regions according to the electronic controlling mechanism: diffusive region, mixture region, ballistic-like region. Fig. 4.3(c g) shows the I-V curve at different temperatures from these three temperature regions. In the diffusive controlling region, the I-V curve at temperature of 200 K or 160 K shows a good linear behavior. Conventionally, a dc I-V curve was used to identify the threshold, or the critical electric field,  $E_{\rm C}$  of the CDW [18,19,29]. The I-V curve of materials with CDW ground state usually behaves as a linear relationship when the current is small, which corresponds to a constant differential resistance dV/dI. As the applied electric field exceeds a threshold, the dV/dI becomes significantly decreased with the continuous increasing applied electric field and enters a nonlinear I-V regime. However, we did not observe such a nonlinear I-V curve at 90 K. One of the reasons may be due to the high electrical conductance of the Cu<sub>2</sub>Se sample we measured (~0.02  $\Omega$ ), so the highest electric field that could be applied is limited by the constant current source. Currently, the highest electric field is only  $3 \times 10^{-5}$  V cm<sup>-1</sup>, which is much less than a typical  $E_{\rm C}$  of  $8.7 \times 10^{-2}$  V cm<sup>-1</sup> for Nb<sub>3</sub>Se [29] and 1.2 V cm<sup>-1</sup> for (TaSe<sub>4</sub>)<sub>2</sub>I [18]. We also made another thinner Cu<sub>2</sub>Se sample with a 10 times larger electrical resistance (~0.2  $\Omega$ ) and raised the applied electric field to  $\sim 3 \times 10^{-4}$  V cm<sup>-1</sup>. However, we still did not observe the decrease in differential electrical resistivity with the increasing applied electric field. As we continued to measure the I-V curve at lower temperatures, a wave-like I-V curve was observed near 50 K with a period of ~100  $\mu$ A and amplitude of 2  $\mu$ V, as shown in Fig. 4.3(c). A negative differential resistance dV/dI at each wave was identified. To our best knowledge, such regular oscillations in *dc* I-V curve have not yet been reported in Cu<sub>2</sub>Se or in other materials.

Fig. 4.4 shows the powder XRD patterns of the nanocomposite Cu<sub>2</sub>Se with 2% Zn, 10% Ni, and 10% Te doped samples along with the parent compound, which were made by the same fabrication process. The XRD measurements were performed on the same Bruker D2 PHASER system as mentioned previously at room temperature. The XRD patterns and subsequent refinements show that the  $\alpha$ -Cu<sub>2</sub>Se exhibits a layered and monoclinic structure where the structure maintains unaffected by different dopants. Fig. 4.5 shows typical SEM images of the Cu<sub>2</sub>Se hot pressed (HP) compound measured by JEOL JSM-6340F Field Emission Scanning Electron Microscope, and the dimensions of the grain sizes are on the order of several microns and are comparable with the grain dimensions for other doped samples. The typical grain size of cold pressed sample is on the order of 100 nm, also shown in Fig. 4.5.



Fig. 4.4: Room temperature XRD patterns of as-prepared Cu<sub>2</sub>Se hot pressed samples with different dopants (2% Zn, 10% Ni, and 10% Te) and parent compound; all of them have similar patterns (peaks).



Fig. 4.5: SEM images of Cu<sub>2</sub>Se parent compound reveal the typical grain size. (a) Cu<sub>2</sub>Se HP parent compound; (b) 2% Zn doped HP sample; (c) 10% Ni doped HP sample; (d) 5% Te doped HP sample, note that in other part of this Chapter it is always 10% Te doped because the 10% Te sample is not cracked and is better for transport measurements but it lacks the SEM image. I

believe the SEM of 10% Te doped sample will be very similar to the 5% Te doped one; (e)  $Cu_2Se$  CP parent compound, it is obvious its grain size is much smaller than others; (f)  $Cu_2Se$  CP + annealing parent compound, grains merged and their sizes are comparable to HP samples but with more vacancies because the annealing happened in the vacuum.

Fig. 4.6 shows the transport properties of these  $Cu_2Se$  samples. In Fig. 4.6(a), the electrical resistivity curves of Cu<sub>2</sub>Se, Cu<sub>1.98</sub>Zn<sub>0.02</sub>Se and Cu<sub>1.9</sub>Ni<sub>0.1</sub>Se show a significant broad maxima around 100 K, which may be attributed to the possible formation of CDW [13-15], however the phenomenon is not visible in the  $Cu_2Se_{0.9}Te_{0.1}$  sample (further discussed in the next section). Compared with the electrical resistivity results of single crystals during CDW transitions, nanostructuring broadens the peak and extends the phase transition to a wider temperature range [16-18]. The occurrence of a CDW and the accompanying Peierls distortion result from the perfect nesting on the Fermi surface and the subsequent partial disappearance of the Fermi surface, as a result the carrier concentration should have a decrease during the transition, and the scattering mechanism will be different from those outside the transition range [19]. Fig. 4.6(c) and Fig. 4.6(e) show the temperature dependence of mobility and Hall carrier concentration from the Hall measurements. As seen in Fig. 4.6(c), the slope of the curves has a significant decrease in the transition range, while maintaining nearly the same character outside of it. We conclude that the scattering originates from the same mechanism outside of the transition, but is altered by the formation of a CDW during the transition. Fig. 4.6(e) further confirms the transition by revealing the decrease of carrier concentration at this temperature range.

Fig. 4.6(b) and Fig. 4.6(d) show the total thermal conductivity and Seebeck coefficient vs. temperature, unlike the broad maxima revealed in the electrical resistivity data, there are no similar anomalies observed in thermal conductivity and Seebeck data. As reported in the literature, Cu<sub>2</sub>Se is a *p*-type electrical conductor with a Cu deficiency in the lattice which results in an equivalent concentration of holes [10,14]. The 10% Ni doped sample shows evidence of similar hole doping behavior to the Cu deficiency because the Ni doping promotes an increased hole concentration due to the number of valence electrons available in Ni. By the Ni doping the carrier concentration is increased and, as a result, Cu<sub>1.9</sub>Ni<sub>0.1</sub>Se has a lower electrical resistivity and higher thermal conductivity compared with other samples. While 2% Zn and 10% Te doping more behave as scattering centers, thus these two doped samples have higher electrical resistivity and lower thermal conductivity. Fig. 4.6(f) and Fig. 4.6(h) show the temperature dependence of the power factor and figure of merit (ZT), and the best thermoelectric performance is from the parent compound, which has a ZT value of 0.14 at 200 K. Fig. 4.6(g) shows the comparison between Cu<sub>2</sub>Se parent compound and *p*-type bismuth antimony single crystal [20], which is a conventional low temperature p-type TE material, and we can see that Cu<sub>2</sub>Se has a better performance at low temperature.



Fig. 4.6: Temperature dependent behaviors of thermoelectric transport properties. (a) Electrical resistivity. (b) Total thermal conductivity. (c) Mobility plotted in *log* scale. (d) Seebeck coefficient. (e) Hall carrier concentration. (f) Power factor. (g) Comparison of ZT between Cu<sub>2</sub>Se nanocomposite parent compound and conventional low temperature *p*-type bismuth antimony single crystal. (h) Figure of merit. Except (g) all other figures have the same legend. The bismuth antimony data is taken as a comparison from ref. [20].

The good thermoelectric performance of α-Cu<sub>2</sub>Se is due to its low dimensional layered structure combine with a ball milling and hot press fabrication process. This results in low thermal conductivity across a wide temperature range T < 300 K. Unlike the structural transition from  $\alpha$ -Cu<sub>2</sub>Se phase to  $\beta$ -Cu<sub>2</sub>Se phase, which appears at ~130 °C in single crystals, the Peierls distortion manifests as a broad peak in both doped and undoped nanocomposite materials and looks like a "weak" phase transition compared with the higher temperature structural transition. Evidence of the Peierls distortion comes from the collective behavior of the many nanocomposite grains and is influenced by the grain size distribution. Our data from thermal conductivity and Seebeck coefficient does not show evidence of a Peierls distortion because this is a weak transition, however this is not the case for such anomalies observed in the structural transition at higher temperatures [12].

## 4. *dc* I-V Curve Measurements and Doping Effects

Fig. 4.7 shows more I-V curves of  $Cu_2Se$  near 50 K measured under different conditions. Fig. 4.7(a) shows that the wave-like I-V curve is repeatable, not a one-time result, in which the second measurement is conducted several days after the first

measurement and with a little shift compared with the first one. In the second measurement, shown in Fig. 4.8(a), the I-V curves at four different temperatures of 200 K, 120 K, 50 K, and 30 K were measured. Only the I-V curve near 50 K shows the notable wave-like feature, while the ones measured at 120 K and 200 K only show normal linear relationship. It is noted that the I-V curve at 30 K still reveals a weak oscillation as shown in the Fig. 4.8(a). In order to confirm our measurement, we prepared another thin sample with resistance of 0.2  $\Omega$  as shown in Fig. 4.7(b). For the thin sample a narrower temperature range was detected. The wave-like I-V curves were observed at the temperatures of 50 K, 48 K, and 30 K, but not at 52 K and 90 K. Furthermore, the period of the oscillation is increased as the temperature decreases from 50 K to 30 K. It is suggested that the regular oscillation is highly sensitive to the temperature. On the other hand, the amplitude of the oscillation of the thin sample  $(0.2 \Omega)$  is smaller than the thick one (0.02  $\Omega$ ), *i.e.*, the differential resistance or resistivity drops below zero for 0.02  $\Omega$ while it is still positive for 0.2  $\Omega$ , which suggested that the phenomena we observed is also sample size related. In order to exclude the possibility that the signal we observed may have come from the equipment, we have done a similar I-V curve measurement for a standard resistor (1  $\Omega$ ) from 30 K to 200 K, but we did not find any wave-like I-V curves, or any noise-like I-V curves, but only perfect linear I-V curves, e.g. at 50 K; more details

will be shown in the next supplementary section.



Fig. 4.7: Regular oscillations of I-V curves in the CDW ground state of Cu<sub>2</sub>Se polycrystalline. (a) Repeatable wave-like I-V curve of Cu<sub>2</sub>Se measured at 50 K for the thick sample with resistance of ~0.02  $\Omega$ , (b) I-V curves at different temperatures for the thin Cu<sub>2</sub>Se sample with resistance of ~0.2  $\Omega$ , which are artificially shifted by 10 µV for 48 K, 20 µV for 50 K, 30 µV for 52 K, and 40 µV for 90 K to separate the I-V curves, respectively, (c) weak magnetic field effect on the I-V curve of the Cu<sub>2</sub>Se measured at 50 K for the thick sample with resistance of ~0.02  $\Omega$ , (d) effect of the applied large current on the I-V curve of the thin Cu<sub>2</sub>Se sample measured at 50 K.

The effect of the magnetic field and the electrical field on the wave-like I-V curve was further investigated, as shown in the Fig. 4.7(c - d). Under the magnetic field of 9 T, the period and amplitude of the oscillation in the I-V curve is nearly unchanged when the current is less than 500  $\mu$ A. According to the shift shown in Fig. 4.7(a), the superposition of the beginning part of two curves in Fig. 4.7(c) is better regarded as a coincidence. It seems that the shift cannot be eliminated; the measurements were performed on the third sample (0.03  $\Omega$ ) as shown in Fig. 4.8(b), and the shifts were still observed. However, the oscillation period decreases slightly when the current is higher than 500 µA. It seems that the electrical field may play a more important role in changing the electronic transport behaviors in CDW ground state. We have applied electric field of  $1.5 \times 10^{-4}$  V cm<sup>-1</sup> on the thin sample (0.2  $\Omega$ ) over 5 hrs. at 50 K, and then re-measured the I-V curve. Surprisingly, the wave-like feature in the I-V curve disappeared, as shown in Fig. 4.7(d).



Fig. 4.8: (a) Second measurement of the I-V curves of the Cu<sub>2</sub>Se thick sample (~0.02  $\Omega$ ) with artificially shifted by 5  $\mu$ V for 30 K, 10  $\mu$ V for 50 K, 15  $\mu$ V for 120 K, and 20  $\mu$ V for 200 K to separate the I-V curves, respectively. (b) Measurements of I-V curves of the third Cu<sub>2</sub>Se hot press sample (~0.03  $\Omega$ ) by Keithley 2182A nanovoltmeter. The figure shows an obvious shift between the two measured I-V curves of the third Cu<sub>2</sub>Se sample (~0.03  $\Omega$ ), however, the oscillation period and amplitude are similar.

It is well-known that a noise-like fluctuation in the dV/dI was widely observed in the NbSe<sub>3</sub>, TaS<sub>3</sub>, and  $K_{0,3}MoO_3$  as a result of the collective moving of the CDW when the applied electric field is higher than the critical field  $E_{\rm C}$  [17,28,30]. However, the applied electrical field in our measurement is far less than the threshold value  $E_{\rm C}$ . The oscillation we observed is very regular, rather than an electronic noise. Another noticeable phenomenon is the Shapiro steps in the dc I-V curves when an rf-frequency ac signal was applied to the samples [15,38-40]. However, these steps can only be observed when the *ac* signal is nonzero due to its interference nature. The Shapiro steps do create a fluctuation in the differential resistance dV/dI, but not a negative dV/dI. Furthermore, the amplitude of the sub-harmonics decreases with an increasing dc electric field. In contrast, our measurement is only conducted under stable dc electric field step by step with a step current of 5 µA. At each step, a waiting time of 15 sec was set to wait for the voltage value becoming stable in our constant current measurement mode. The amplitude and period of the wave we observed did not show a notable decay with increasing current. Furthermore, a negative differential resistance was observed at each wave peak. One of the mechanisms for the wave-like I-V curve could be related to the special periodic modulation of the electronic charge density in CDW ground state, and also to the formation of electron-hole pairs due to the nesting on the Fermi surface, which may result

in a local carrier concentration, or carrier mobility jump as the Fermi energy across the gap with rising applied *dc* electric field. We note that the negative differential resistivity phenomenon has been observed in a molecular conductor, in which a ballistic mechanism is dominant in the electronic transport [42]. Recently, a negative differential resistivity was also reported in a CDW material BaIrO<sub>3</sub> single crystal at 4.2 K [43]. However, only one peak was observed in Nakano's I-V curve. The observed negative differential resistivity in Cu<sub>2</sub>Se, which is related to a regular applied electric field, is still unique. We believed that the onset of oscillation (wave-like fluctuation) of I-V curve in Cu<sub>2</sub>Se should be a new material-related phenomenon. Although the oscillation looks like real, the negative resistance appeared in  $1^{st}$  measurement in Fig. 4.8(b) below 50 µA is better regarded as an experimental artifact.



Fig. 4.9: Temperature dependent electrical properties of Cu<sub>2</sub>Se with different dopants: (a) electrical resistivity, (b) carrier concentration, (c) I-V curves of sample Cu<sub>1.98</sub>Zn<sub>0.02</sub>Se, (d) differential resistance dV/dI of Cu<sub>1.98</sub>Zn<sub>0.02</sub>Se at 40 K. The I-V curves in (c) are artificially shifted by 3  $\mu$ V for 35 K, 6  $\mu$ V for 40 K, 9  $\mu$ V for 45 K, 12  $\mu$ V for 50 K, and 15  $\mu$ V for 55 K to separate the I-V curves.

Fig. 4.9(a) shows the doping effect on CDW of Cu<sub>2</sub>Se. The first investigation was to add extra Se (which is equal to the Cu deficiency) to increase the hole concentration from  $2.1 \times 10^{20}$  cm<sup>-3</sup> to  $2.5 \times 10^{20}$  cm<sup>-3</sup>. A similar "hump" in the electrical resistivity was seen throughout the Peierls transition but the temperature was increased from 125 K to 138 K. We also note that in an early work on p-type Cu<sub>1.7-1.8</sub>Se ( $p = 3.0 \times$  $10^{21}$  cm<sup>-3</sup>) the data shows a similar but irreversible "hump" in electrical resistivity near 180 K [15]. It seems that the increased carrier concentration could influence the transition temperature. Recently, a theoretical study suggested that a phase transition due to the CDW may exist in Cu<sub>2</sub>Se near 120 K [15]. Zn has one more valance electron than Cu, while Ni has one valance electron less than Cu, both of which will significantly change the carrier concentration of the Cu<sub>2</sub>Se. Both samples with Zn and Ni doping have shown notable Peierls transition near 130 K, which is slightly higher than the pure Cu<sub>2</sub>Se, and resulted in a carrier concentration and mobility decrease near the Peierls transition as shown in the Fig. 4.9(b). Furthermore, Cu<sub>1.98</sub>Zn<sub>0.02</sub>Se has the largest electron-phonon coupling constant of 0.65, while Cu<sub>1.9</sub>Ni<sub>0.1</sub>Se has the largest saturated energy gap of 61.2 meV. The way Zn and Ni influencing the CDW is different from the Cu vacancy. Besides tuning the electrons, we also partially substituted the Se with Te allowing for increased phonon scattering and also breaking the perfect nesting on Fermi surface. No evident

Peierls transition was seen in the sample Cu<sub>2</sub>Se<sub>0.9</sub>Te<sub>0.1</sub>. The suppression of propagation phonon owing to the alloying effect breaks the electron-phonon coupling, meanwhile the substitution of Se by Te in the lattice structure results in the removal of the induced subsequent lattice instability. Fig. 4.9(c) shows the I-V curve of the sample  $Cu_{1.98}Zn_{0.02}Se$ which is conducted over a wide temperature range, and a similar wave-like fluctuation was still observed at the temperature below 40 K. It seems that the onset temperature of wave-like fluctuation is sensitive to the dopants. The derived wave-like dV/dI curve of  $Cu_{1.98}Zn_{0.02}Se$  at 40K, from which we clearly see a negative differential resistance, is shown in the Fig. 4.9(d). All the relevant derived parameters are summarized in Table 4.1. We still have no idea about the clear picture of this negative differential resistance. However, we believed what our observation is a material-related new phenomena, which could be a new quantum effect or strong electron-phonon coupling effect in the CDW ground state. Such wave-like fluctuation in the I-V curve may provide a new way to probe the new electronic transport phenomena of the CDW ground state.

Table 4.1: Charge-density wave related Peierls transition temperature  $T_P$ , saturated energy gap  $E_{\Delta}$ , electron-phonon coupling constant  $\lambda$ , and the temperature  $T_{wave}$  observing the wave-like fluctuation in the I-V curve.

Sample	<i>Т</i> <sub>Р</sub> /К	$E_{\Delta}/\mathrm{meV}$	$\lambda$ /dimensionless	$T_{\rm wave}/{\rm K}$
Cu <sub>2</sub> Se	125	40.9	0.54	50
Cu <sub>2</sub> Se-Zn	131	54.8	0.65	40
Cu <sub>2</sub> Se-Ni	128	61.2	0.63	n.a.
$Cu_2Se_{1.02}$	138	40.4	0.51	n.a.

n.a.: not available right now.

## 5. Supplementary Materials for *dc* I-V Curve Measurements

Fig. 4S.1 shows a *dc* I-V curve measurement of a 1-ohm standard resistor at 50 K, in order to make a comparison between the Cu<sub>2</sub>Se sample and the resistor. As we see the I-V curve of the resistor is a perfect line throughout the whole current range, rather than the oscillations shown up in our Cu<sub>2</sub>Se samples. The voltage does not reach 1000  $\mu$ V when the current is 1000  $\mu$ A, *i.e.* the resistance is smaller than 1  $\Omega$ , because the resistor changes its resistance when temperature goes down.



Fig. 4S.1: The I-V curve of the 1  $\Omega$  standard resistor at 50 K, and a straight line was observed. It behaves in a perfect linear relationship, which makes us conclude that the wave-like fluctuation is the effect from the polycrystalline sample, not from the measuring circuit.

## 6. Results of Ag Doped Cu<sub>2</sub>Se Compound

As mentioned previously, using Ag as a dopant into  $Cu_2Se$  is not a good idea, because Ag produces electron into the *p*-type  $Cu_2Se$  although Ag and Cu are usually isoelectronic. This part is a data recording, and presents some results which are not suitable in the main text. The structure of CuAgSe is different from Cu<sub>2</sub>Se and Ag atoms do not evenly substitute Cu atoms [44], but here I just simply regard CuAgSe as 50% Ag doped Cu<sub>2</sub>Se. Because Ag does not improve the thermoelectric performance of Cu<sub>2</sub>Se and also Ag is much more expensive than other dopants, we do not deeply investigate the properties of Ag doped Cu<sub>2</sub>Se, Fig. 4.10 shows some transport results of Cu<sub>1.9</sub>Ag<sub>0.1</sub>Se we got from our experiments.



Fig. 4.10: Transport properties of hot pressed (HP) Ag doped Cu<sub>2</sub>Se nanocomposites, the CuAgSe (*i.e.* 50% doped) polycrystalline data is adapted from ref. [44]. (a) Electrical resistivity; (b) Seebeck coefficient; (c) Thermal conductivity; (d) Derived figure of merit; (e) Mobility; and (f) Carrier concentration; note that (e) and (f) are plotted in *log* scale. As usual, the carrier concentration data is calculated from the Hall coefficient  $R_{\rm H}$ .  $R_{\rm H}$  can be either positive (*p*-type) or negative (*n*-type) according to the type of carriers, however, its absolute value is used to derive the concentration and thus lose the information of carrier type.



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In Fig. 4.10(a) we see that  $Cu_{1.9}Ag_{0.1}Se$  has a lower electrical resistivity than other samples, this could be explained by its extremely large carrier concentration at low temperature. However, when temperature increases the concentration decreases significantly and becomes one half of the value of other samples. Normally this would indicate a higher electrical resistivity, but from Fig. 4.10(a)  $Cu_{1.9}Ag_{0.1}Se$  still has the lowest resistivity at room temperature. This "paradox" could be solved by using a different model to calculate carrier concentration.


Fig. 4.11: An illustration of 4-probe yx-measurement. The sign of voltage across the sample depends on the type of carriers, which is different from the 4-probe xx-measurement where the voltage is always positive unless the wires are connected incorrectly or the resistance is out of range.

Fig. 4.11 shows an illustration of a Hall measurement, by measuring the Hall resistance  $V_y/I_x$  or the Hall resistivity  $\rho_{yx}$  if further considering the dimensions of the sample; one is able to calculate the Hall coefficient  $R_{\rm H}$  by the definition

$$R_{\rm H} = \frac{V_y}{I_x} \frac{t}{B} = \frac{\rho_{yx}}{B}$$

$$\tag{4.5}$$

where t is the thickness and B is the magnetic field. As a result  $R_{\rm H}$  is always correct because it is from the definition. But the derivation of carrier concentration n from  $R_{\rm H}$ is model-sensitive; we can have different explanations of  $R_{\rm H}$  depending on different models we choose. In the simplest case, the Drude model by assuming there only exists one type of carrier, one is able to have the commonly accepted result  $R_{\rm H} = 1/n_e$ , and this is the formula we use to extract n most of time.

S. Ishiwata *et al.* used a two-carrier model to interpret their CuAgSe polycrystalline results [44], this two-carrier model may satisfy our  $Cu_{1.9}Ag_{0.1}Se$  sample but we lack enough data to examine it, what we can conclude is that the simple model and derived carrier concentration of  $Cu_{1.9}Ag_{0.1}Se$  may not be correct. The Hall effect is the average effect of both carriers, so it is a subtraction and reduces the concentration value. But in the transport process both of them can conduct heat and charge, so their

contribution becomes a sum, and this is confirmed by the electrical resistivity and thermal conductivity measurements shown in Fig. 4.10(a) and Fig. 4.10(c).

Another interesting thing to mention is the crossover from *p*-type to *n*-type and vice versa. As stated previously, Cu<sub>2</sub>Se is *p*-type while both Ag<sub>2</sub>Se and CuAgSe are *n*-type. So there must be a transition from *p*-type to *n*-type if we dope Cu<sub>2</sub>Se with Ag. Normally, the sign (or the type) of the majority carriers is determined by Hall measurements, and is further confirmed by the Seebeck coefficient. In Fig. 4.10(b) we clearly see that CuAgSe has a negative Seebeck coefficient which is consistent with its Hall measurements. However, the situation is quite different for Cu<sub>1.9</sub>Ag<sub>0.1</sub>Se and it looks like Cu<sub>1.9</sub>Ag<sub>0.1</sub>Se is around the crossover.

From Fig. 4.10(b) we can see the trend  $Cu_2Se \rightarrow Cu_{1.9}Ag_{0.1}Se \rightarrow CuAgSe$ , the doping of Ag presses the Seebeck curve down and finally changes the sign, but it's still positive for  $Cu_{1.9}Ag_{0.1}Se$ , *i.e.*  $Cu_{1.9}Ag_{0.1}Se$  is still *p*-type if we just consider the sign of the Seebeck coefficient. However, our Hall measurements propose a different scenario, as shown in Fig. 4.12.



Fig. 4.12: Temperature dependent Hall coefficient of  $Cu_{1.9}Ag_{0.1}Se$  sample, with no doubt is negative and the sample shows electron dominance.

Now things become a little complicated. A single measurement cannot uniquely determine whether a material is *n*-type or *p*-type. Most of time the Hall measurements and Seebeck measurements are consistent, but in the crossover regime resulting from the fact that the dopant does not improve the original carriers but compensates them, these two measurements may contradict with each other (as the example of  $Cu_{1.9}Ag_{0.1}Se$ ). I think the reason may be that different carriers (electrons and holes) have different responses to the applied magnetic field and thermal gradient. But Hall measurement is more common than Seebeck measurement in the lab because it is not a thermal measurement, so it looks like the Hall measurement is the "industrial standard" to determine the type of a material in the lab (I guess and it is not confirmed). But due to the compensation of these carriers in the transport processes, such kind of materials can never be a good thermoelectric material candidate, as shown in Fig. 4.10(d),  $Cu_{1,9}Ag_{0,1}Se_{1,1}$ has the lowest figure of merit (even lower than CuAgSe [44]), so it is not a problem in the thermoelectric area where people are always trying to increase the TE performance.

Similar to  $Cu_2Se_{0.9}Te_{0.1}$ ,  $Cu_{1.9}Ag_{0.1}Se$  also does not show a nonlinear "hump" in its electrical resistivity measurement. The explanation is similar, because Se and Te are isoelectronic, so do Cu and Ag, the band structure changes significantly and destroy the perfect nesting on the Fermi surface.

### 7. Conclusions

A Peierls transition was identified in polycrystalline Cu<sub>2</sub>Se near 125 K according to the nonlinear electrical resistivity, the carrier concentration and also the carrier mobility. The characteristic parameters of the charge density wave in the polycrystalline Cu<sub>2</sub>Se was calculated to show a saturated energy gap  $\Delta$  of 40.9 meV at zero temperature, the electron-phonon coupling constant  $\lambda$  of 0.6 and the coherent length of electron-hole pair of  $\xi_0 \sim 1$  nm. After entering the new CDW ground state below 90 K, a negative differential resistivity was identified with a regular oscillation of the I-V curve. The regular oscillation in dc I-V curve was not magnetic field sensitive, but temperature and sample size sensitive. The wave-like fluctuation is different from the conventional electronic noise observed above the threshold field  $E_{\rm C}$ , and also the Shapiro steps with a finite applied ac field. Both the Zn and Ni doped Cu<sub>2</sub>Se show CDW characters with increased energy gap and electron-phonon coupling constant. No notable Peierls transition was identified from the temperature dependent resistivity and Hall measurement in Te doped Cu<sub>2</sub>Se. This reveals that the transition could be tuned by

different dopants. Similar wave-like I-V curve was also seen in the  $Cu_{1.98}Zn_{0.02}Se$  near 40 K, which suggests that the onset of wave-like fluctuation of I-V curve in  $Cu_2Se$  should be a material-related new phenomenon. The best *ZT* value of 0.14 at 200 K is achieved from the parent compound due to its unique structure and the distinctive fabrication processes, which is higher than the performance of the conventional low temperature *p*-type bismuth antimony single crystals. This confirms the potential applications of  $\alpha$ -Cu<sub>2</sub>Se as a *p*-type thermoelectric material in the low temperature field.

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# Chapter V: Induced Electronic Anisotropy in Bismuth Thin Films through Angle-Dependent Magnetoresistance Measurements

### 1. Introduction

Bismuth (Bi) has recently received renewed interest because it is a key ingredient of many thermoelectric materials [1-3], topological insulators [4], and valleytronic materials [5]. Bi is a semimetal with a small band overlap of ~38 meV at cryogenic temperatures and has highly anisotropic electron effective masses [6,7] of ~200. The large band mass anisotropy makes Bi a good material platform for studying very heavy and light electrons simultaneously. When alloyed with small concentrations of antimony (Sb), a bandgap opens, causing  $Bi_{1-x}Sb_x$  to become an excellent low temperature thermoelectric, with its peak figure of merit (*ZT*) occurring near the boiling temperature of liquid nitrogen [1]. Therefore, Bi and  $Bi_{1-x}Sb_x$  remain promising candidates for cryogenic Peltier coolers.

While previous studies have focused on bulk single crystalline samples, nano-structures offer a route to create higher *ZT* materials [8]. Nano-structuring has

been shown to be effective in increasing phonon scattering, while having a lesser impact on degrading electronic transport [3,9]. As a result, the previous literature on Bi and  $Bi_{1-x}Sb_x$  has investigated nanowires [10], thin films [11], nanoporous thin films [12] and nanocomposites [3]. Despite numerous studies on nanostructured Bi, there have been few works on investigating the effects of crystalline texture and order on electrical and thermal conduction. Recently, it was theoretically shown that different band structures could be derived from Bi or  $Bi_{1-x}Sb_x$  films grown in different crystal orientations [13]. Some of the resulting band structures were highly anisotropic, a desirable property for thermoelectrics. Therefore, it is expected that the degree of anisotropic electrical conduction in a thin polycrystalline film of Bi will depend on the collective crystalline orientation of its grains.

#### 2. Experimental Details

Bismuth thin films were evaporated using either thermal evaporation or molecular beam epitaxy. In the case of thermal evaporation, films were evaporated at a rate of 0.2 Å/s, as monitored by a quartz crystal monitor. Mica substrates were freshly cleaved. Amorphous SiO<sub>2</sub> on Si substrates were made by dry oxidation of SiO<sub>2</sub> and were cleaned using a standard RCA cleaning method to remove any metallic or organic surface contaminants. Both the mica and SiO<sub>2</sub>/Si substrates were heated in high vacuum at  $\sim$ 120 °C before and during deposition. Film thicknesses were checked using atomic force microscopy. Contacts were made using indium dots, which were able to punch through the thin native oxide layer on the films. Wires were secured to the indium dots using silver paint. We also tried the sapphire substrates which are expensive, but the results showed that the Bi film was also non-textured.

To check the crystallinity of the grains, both transmission electron microscopy (TEM) and x-ray diffraction (XRD) measurements were used. Using TEM, we are able to resolve the lattice structure in Fig. 5.1(a). The trigonal axis points out of plane, while the structures of individual grains are rotated with respect to each other. Through XRD measurements, we were able to resolve thickness fringes shown in Fig. 5.1(b), indicative that the crystal lattice is preserved from the top to bottom of the film.



Fig. 5.1: (a) Planar TEM image of textured Bi film. Most grains are >100 nm. The insets provide higher resolution images of two different grains showing that they are rotated with respect to each other. (b) XRD spectrum of the trigonal peak (0003) showing side thickness fringes. Other peaks come from the substrate.

The electronic transport measurements were performed using a rotator option of Physical Properties Measurement System (PPMS) from Quantum Design. The sample was connected by using a standard 4-probe Van der Pauw method since we were dealing with the thin films. When rotating the rotator, the angle  $\theta$  used here is the same angle used in PPMS, describing the deviation of the sample carrier from the horizon position. Because the applied field is vertical (upward positive) so when the angle is zero, the field is perpendicular to the film and substrate, shown in Fig. 5.2.





### $0^{\circ}$ sample $\perp$ field

## $90^{\circ} sample \parallel field$

Fig. 5.2: The orientation of the experimental setup. The angle used here describes the position of the sample carrier holder with respect to the horizon, but the applied magnetic field is always vertical and upward positive, as a result 0° means the field is perpendicular to the sample while 90° means parallel.

Due to the existence of the applied magnetic field and the different rotational axis, there are basically two different configurations of the Van der Pauw connection, as shown in Fig. 5.3. These two configurations are the most important configurations of the Van der Pauw method, namely vertical and horizontal configuration respectively. The final sheet resistance and electrical resistivity are derived according to the above results at different angles.



Fig. 5.3: Two different configurations of the Van der Pauw connection. In configuration 1 the current is perpendicular to the field only at 0°, while in configuration 2 they are always perpendicular with each other, at any angles.

### 3. Structural Characterization

In this Chapter, we characterize and compare electronic transport in Bi thin films with texture (*i.e.* films having grains with preferential crystalline orientations) versus thin films without texture. We control the texture of Bi thin films, deposited using thermal evaporation or molecular beam epitaxy, by using different supporting substrates. In this study, we primarily focus on films grown on top of crystalline mica (001) or amorphous SiO<sub>2</sub> substrates. Films were deposited via thermal evaporation at  $\sim 1 \times 10^{-8}$  Torr, at a rate of 0.1 - 0.2 Å/s and a substrate temperature of ~120 °C. We monitor the texture and crystallinity of the films using X-ray diffraction (XRD) and check the surface roughness and grain shape with atomic force microscopy (AFM). The AFM image in Fig. 5.4(a) shows that each grain grows into a triangular shape suggesting that the film has texture. This is confirmed through the XRD spectrum shown in Fig. 5.4(c), where all of the observed peaks correspond to the (0001) direction, indicating growth of a textured polycrystalline film where the trigonal axis points out of the plane of the film. From transmission electron microscope (TEM) measurements, we measure the grain sizes to be  $\sim 200 - 500$  nm, and observe that while all grains are grown normal to their trigonal axes, their in-plane grain structures are rotated randomly with respect to each other. Thickness

fringes are observed, which confirm that the grains maintain the same preferred trigonal crystalline orientation resulting from the growth substrate interface to the top surface of the film. In contrast, the AFM image in Fig. 5.4(b) shows that the surface of Bi deposited on SiO<sub>2</sub> now contains several different shapes in addition to triangular ones. The corresponding XRD spectrum in Fig. 5.4(d), exhibits many more peaks than Fig. 5.4(c), indicating that the polycrystalline film no longer has a preferred trigonal axis texture, but is made up of grains with randomly oriented crystalline directions. In this study we focus on thin films with thicknesses (<80 nm) much smaller than the average grain size in order to ensure that the longest electron mean free path is in the plane of the film. We also note from AFM measurements that the textured samples tend to have a root mean square (RMS) intra-grain surface roughness of ~1 nm. By comparison, non-textured samples have an RMS intra-grain surface roughness of ~1.5 nm.



Fig. 5.4: (a) and (b) Atomic force microscope images of a textured and a non-textured film. The grains in the textured film appear primarily as triangles (traced by blue dashed lines) on the surface. By contrast, the grains in the non-textured film produce a more diverse collection of shapes (traced by red dashed lines) on the sample surface. (c) and (d) X-ray diffraction (XRD) spectra of textured and non-textured samples. The textured sample is oriented with its trigonal axis normal to the plane of the film. The numerous peaks in the non-textured film XRD spectra indicate the presence of many different crystalline orientations.

## 4. Angle-Dependent Electronic Transport Measurements in Applied Magnetic Field

We measure magnetoresistance (MR) from 3 to 300 K in a Quantum Design Physical Properties Measurement System (PPMS) cryostat while rotating the films in a 9 T magnetic field for the two different configurations, shown schematically in Fig. 5.5(a). Films were also measured in a Hall bar geometry, but no appreciable difference in these measurements were observed relative to those done in the Van der Pauw geometry. In what we denote as configuration 1, the current is applied such that as the film is rotated, the angle between the current flow direction and the magnetic field changes. In configuration 2, the current is applied such that it is always kept perpendicular with respect to the magnetic field. In these measurements we rotate samples by 360° with an incremental step size of 3°, to ensure that there is no misalignment between the film and the magnetic field. The resistance in configuration 1,  $R_{C1}$ , shown in Fig. 5.5(b), reaches a minimum when the film is parallel to the field (when the rotator is oriented at 90° and 270°). At these angles,  $R_{C1}$  is approximately equal to the zero-field resistance at each respective temperature, indicating that there is negligible MR when the current and field are aligned. As we tilt the sample, and the angle between the field and the plane of the

film increases, the component of the field perpendicular to the film also increases. Thus  $R_{C1}$  reaches its maximum value when the field is normal to the plane (*i.e.* when the rotator is at 0° or 180°). Our observation of a large change in MR is consistent with other measurements in bulk Bi [14], thin films [15] and nanowires [16]. We note that quantum oscillations have not been observed in the present work, because of the polycrystalline nature of the films. In configuration 2, the magnitude of the magnetic field normal to the current flow remains constant during rotation. Instead, changing the angle between the film plane and the magnetic field tunes the degree of contribution between surface and grain boundary scattering. When the film is oriented perpendicular to the field, the cyclotron orbit is in the plane of the film so that the dominant scattering mechanism is grain boundary scattering. When the film is oriented parallel to the field, the carriers are pushed towards the surface of the film, thereby increasing surface scattering. Therefore, the observed resistance in configuration 2,  $R_{C2}$ , reaches its maximum when the plane of the film is parallel to the field, in agreement with expectations. Fig. 5.6 shows the compensation between the boundary scattering and surface scattering in the thin film, of course the relative size of the grains and the thickness of the film determine the contribution to the sheet resistance from the surface scattering.



Fig. 5.5: (a) Schematic of the measurement configuration for  $R_{C1}$  (top-left, current flow rotating with the plane of the film) and  $R_{C2}$  (bottom-left, current flow kept normal to the magnetic field). The left-side shows the schematic from a top down view with the dashed line indicating the axis of rotation. The right-side image gives the cross-sectional view of the measurement setup. (b)  $R_{C1}$  measured as a function of rotator angle for a 77 nm textured thick film in a 9 T field, (c)  $R_{C2}$  measured as a function of rotator angle for the same film in a 9 T field. (d) Extracted resistivity of the film versus rotator angle. Measurements on this film in (b – d) were done over a temperature range of 15 to 300 K in 25 K increments for T > 25 K and in 5 K increments for T < 25 K. For clarity, we only display results for T = 15, 100, 200, 300 K.



Fig. 5.6: Schematic illustration of boundary scattering and surface scattering happened in the bismuth thin film when an external magnetic field was applied. The electrons (or holes) are driven by the Lorentz force to achieve a cyclotron motion and scatter with the grain boundaries in the film or the surface of the film.

We use the Van der Pauw method to extract the resistivity,  $\rho$ , of films using  $R_{C1}$ and  $R_{C2}$ , as shown in Fig. 5.5(d). It should be noted that in a quantitative comparison between Figs. 5.5(b) and 5.5(c),  $R_{C1}$  has a much larger angular dependence than  $R_{C2}$ . Therefore, the angular dependence of  $\rho$  is dictated by  $R_{C1}$ . As a result, plots of  $\rho$ versus  $\theta$  very closely resemble Fig. 5.5(b). We plot, in Fig. 5.7(a), the ratio of the maximum over the minimum value of resistivity,  $\rho_{max}/\rho_{min}$ , taken from the rotation experiment, as a function of temperature for various film thicknesses (3 - 80 nm). At room temperature, electron-phonon scattering is the dominant scattering mechanism and keeps  $\rho_{\rm max}/\rho_{\rm min}$  small. As the temperature is lowered,  $\rho_{\rm max}/\rho_{\rm min}$  reaches a maximum, as electron-phonon scattering is reduced in comparison with other scattering mechanisms, such as impurity scattering. We find that samples with a sharper peak in Fig. 5.7(a), tend to have higher mobility (see discussion below about using eqn. (5.1) to extract mobility), indicative of a purer sample. For all the films, below ~80 K, no temperature dependence is observed in  $\rho_{max}/\rho_{min}$ . This is the temperature range where we will focus the discussion, as it is also the range most relevant to cryogenic Peltier coolers. Focusing on the low temperature regime, we observe that as the thickness of the film decreases,  $\rho_{\text{max}}/\rho_{\text{min}}$  also decreases in a near linear fashion, as seen in Fig. 5.7(b). To understand this trend, the resistivity can be broken up into two components :

 $\rho = \rho_{\rm i} + \rho_{\rm s}$ , where  $\rho_{\rm i}$  is the "intrinsic" resistivity that may vary with magnetic field strength, and  $\rho_{\rm s}$  is the surface scattering component of resistivity which varies with film thickness. As the film thickness decreases, the contribution of surface scattering increases, thereby decreasing the values of  $\rho_{\rm max}$  and  $\rho_{\rm min}$ . This is evidenced in Fig. 5.7(b) as  $\rho_{\rm max}/\rho_{\rm min}$  approaches a value of one at very small thicknesses, indicating that  $\rho_{\rm max} \sim \rho_{\rm min} \sim \rho_{\rm s}$ . Even though  $\rho_{\rm max}/\rho_{\rm min}$  decreases, we are still able to observe curves that qualitatively look the same as Fig. 5.5(c) for films down to thicknesses of 3 nm.



Fig. 5.7: (a) Ratio of the maximum to minimum resistivity extracted from the measurement described in Fig. 5.5(d) versus temperature. The ratio is extracted for films of various thicknesses over a range from 3 to 80 nm. Below ~80 K  $\rho_{max}/\rho_{min}$  is invariant to changes in temperature. (b)  $\rho_{max}/\rho_{min}$  at low temperature (T < 80 K) versus film thickness.

When non-textured films are rotated in a magnetic field, the detected change in resistivity is very small compared to the results for the textured films of similar thicknesses. Fig. 5.8(a) shows the temperature dependence of  $\rho_{max}/\rho_{min}$  for textured films that are 20 and 40 nm thick and for non-textured films that are 25 and 40 nm thick. At temperatures above 200 K, the resistivity of our Bi thin films does not depend on texture, since phonon scattering, which is isotropic, strongly reduces any anisotropic transport. However, we observe a strong deviation in resistivity versus angular orientation dependence for textured versus non-textured films at temperatures <200 K. At cryogenic temperatures,  $\rho_{max}/\rho_{min}$  of non-textured films is smaller than that of textured films.

First we discuss the possibility that different scattering mechanisms are responsible for the observed texture dependent trend. While, the non-textured films do have slightly smaller grains, we keep the film thicknesses about an order magnitude smaller than the grain size in both the textured and non-textured case. In these thin films, surface scattering is the main scattering mechanism, given the strong dependence of resistivity on film thickness. It is worth noting that the low temperature values of  $\rho_{\text{max}}/\rho_{\text{min}}$  for the non-textured 40 nm thick sample are even less than that of the 20 nm thick textured sample. Based on Fig. 5.7(b), we would expect the slightly rougher

non-textured 40 nm thick film's curve in Fig. 5.8(a) to fall between that of the 40 nm and 20 nm thick textured films. To more quantitatively compare the transport between textured and non-textured films, we extract the mobility as a function of film thickness for both types of films in Fig. 5.8(b). To extract the mobility we fit the ordinary magnetoresistance  $R_{C1}$  with the following equation at low field (<0.5 T) where the data is well represented by a quadratic equation [17]:

$$\frac{R_{\rm C1}(B)}{R_{\rm C1}(0)} = 1 + (\mu B)^2$$

(5.1)



Fig: 5.8 (a) Comparison of  $\rho_{max}/\rho_{min}$  versus temperature for textured (solid symbols) and non-textured (open symbols) samples. (b) Extracted peak mobility as a function of sample thickness for both textured (solid symbols) and non-textured (open symbols) samples. The lack of texture does not significantly lower the mobility of these films. (c) Magnetoresistance (MR) as a function of magnetic field strength for a sample oriented parallel (||) and perpendicular ( $\perp$ ) to the magnetic field, and measured on a 20 nm textured film. Symbols represent data and lines represent the fit using eqn. (5.2). (d) MR versus field strength for a parallel and perpendicular oriented 25 nm non-textured film. The inset shows the same plot except for a non-textured Sb film of 45 nm thickness. In contrast to Bi, the MR for the perpendicular orientation in a non-textured Sb has a much reduced MR. Measurements in (c) and (d) are done in the configuration described in Fig. 5.5(a).

The fit for a representative data set is shown in Fig. 5.9. This particular data set was extracted from angular dependence measurement, like the one displayed in Fig. 5.5(b) by multiplying the data by  $cos(\theta)$ . From Fig. 5.9, it is evident that the fit is excellent at fields less than 1 T where the resistance change with magnetic field is well described by ordinary magnetoresistance.



Fig. 5.9:  $R_{C1}$  versus magnetic field. Solid line represents data and dashed lines represent fits using eqn. (5.1).

Using this method, we observe that the mobility,  $\mu$  of textured films and non-textured films do not differ appreciably, as seen in Fig. 5.8(b). Therefore, it is very unlikely that the drop in  $\rho_{\text{max}}/\rho_{\text{min}}$  for the non-textured samples can come from a change in scattering mechanisms.

Since scattering cannot explain the discrepancy in behavior between textured and non-textured samples, we investigated the MR in the films more carefully: we monitored  $R_{C1}$  as we incrementally increased the field. Here, the experiment was conducted in two different film orientations, parallel and perpendicular to the field for both textured and non-textured samples. For the case of a textured film, shown in Fig. 5.8(c), when it is oriented perpendicular to the field, we observe the textbook case of an increasing resistance as a function of field strength. In agreement with previous measurements made on polycrystalline Bi films [18], we observe a much weaker field dependence of the resistance when the textured film is oriented parallel to the field. However, when we measure the non-textured sample in the same manner, we observe the presence of MR in both the perpendicular orientation as well as the parallel orientation, as seen in Fig. 5.8(d). The existence of MR for both orientations indicates that current flow is anisotropic in the non-textured film, a result of preferential current flow along certain crystallographic orientations.

To fit the high field dependence of the MR up to 9 T, we use a simplified Hikami-Larkin-Nagaoka (HLN) formula [19] in the limit of strong spin-orbit coupling, given as

$$\Delta G(B) = -\frac{\alpha e^2}{\pi \hbar} \left[ \psi \left( \frac{\hbar}{4eL_{\phi}^2 B} + \frac{1}{2} \right) - \log \left( \frac{\hbar}{4eL_{\phi}^2 B} \right) \right] + \beta B^2$$
(5.2)

where  $\psi$  is the digamma function,  $\alpha$  is a prefactor,  $L_{\phi}$  is the phase coherence length, and  $\beta$  is the quadratic coefficient which accounts for additional scattering terms. We use eqn. (5.2) to extract the phase coherence length of both films in both the parallel and perpendicular orientations. Fits to data are shown in Fig. 5.8(c) and 5.8(d). For the textured sample, the perpendicular orientation gives a phase coherence length of ~11.4 nm. Interestingly, the parallel orientation exhibits weak localization as the MR slowly decreases as a function of field strength, and we are therefore not able to use eqn. (5.2) to fit to the data. The extracted phase coherence lengths of the non-textured sample are ~121.5 and 15.7 nm for the perpendicular and parallel cases, respectively. Again, the out-of-plane roughness is not interfering with the in-plane conduction, as shown from the fact that the phase coherence length in the textured sample is smaller or close to those
extracted from the non-textured sample. Finally, the large difference in  $L_{\phi}$  for the non-textured samples indicates that the transport in non-textured films is highly anisotropic.

The conductivity of a material depends on the effective mass, density of states, and scattering rates. Compared to the anisotropy of the effective mass, the anisotropy that could be introduced through scattering mechanisms is small. Therefore, we hypothesize that the preferential current flow direction in a crystal grain is dominated by the large mass anisotropy in Bi. To test this hypothesis, we compare our results on Bi with the same measurements that we performed on Sb thin films (see the inset to Fig. 5.8(d)). Unlike Bi, which has a mass anisotropy of  $\sim 200$ , Sb has a mass anisotropy of 6 [6,7]. We use Sb as our control material, as opposed to another metal or semiconductor, because similar to Bi, Sb has the same rhombohedral lattice structure and is also a semimetal [7]. In the inset in Fig. 5.8(d), we observe that the non-textured Sb thin film exhibits a weaker MR when it is oriented parallel to the field. Therefore, it seems that the anisotropic conduction that we observe is a direct result of the large mass anisotropy of the electron effective mass in Bi.

## 5. Conclusions

In conclusion, we have demonstrated that removing texture from Bi thin films can induce anisotropic conduction, giving rise to preferential current flow directions in each grain depending on its crystallographic orientation. Our results show that this preferential current flow occurs for T < 80 K, but not at higher temperatures. At higher temperatures, scattering between carriers and phonons destroys these preferential pathways, thereby making electrical conduction in textured and non-textured films nearly identical. However, for applications operating at low temperature (e.g. cryogenic Peltier coolers operating at 77 K or below), mass anisotropy will give rise to texture dependent effects on electrical transport, especially in materials that have very large mass anisotropy like Bi and Bi<sub>1-x</sub>Sb<sub>x</sub>. Looking forward, control over the arrangement and alignment of the crystalline orientation of individual grains could prove to be technologically important since texturing would allow control over current flow within a material with a single chemical constituent, without the use of external fields.

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# Chapter VI: Conclusions

### 1. Overview

In this section I'm going to quickly sum up the researches have done in the previous chapters, and also one of the works not showing in the main text but in the appendix. Generally speaking, this dissertation is devoted to the study on thermal and electrical transport properties of thermoelectric materials through magnetic field and nanostructuring.

Chapter 1 and Chapter 2 introduced the background of our experimental thermoelectric area, including the theory and the experimental details. Of all the instruments in our lab, the Physical Properties Measurement System (PPMS) is the most important equipment in Opeil's lab. Not only does the PPMS provide a cryogenic temperature circumstance with high precision (within 0.001 K), but also it sets up an adjustable steady magnetic field up to 9 T. With the supplied temperature and field, we are able to perform all kinds of measurements.

Chapter 3 focused on the Lorenz number project, which shows how the magnetic

field affects the electronic thermal conduction and electric conduction of electrons (or holes) in single crystal metals and semiconductors in extenso, while the phononic conductions are presumed to be field independent. Our work successfully shows the suppression of electron transport under applied a strong magnetic field, and achieves the separation of phononic transport from the electronic transport by the field at low temperature regime. The Lorenz ratio of single crystal metals show a deviation from the standard Sommerfeld value in the intermediate temperature regime, mainly due to the inelastic scattering which results in the scattering processes degrading a thermal current but not degrading an electric current (Ashcroft & Mermin), and is well described by the formula provided there. The phononic thermal conductivity of metals cannot be measured directly, however, with the help of successful separation of both thermal conductivities, one is able to see the temperature dependence of phonon thermal conductivity of metals, and its temperature power laws are well verified by our experiments. The semiconductors are quite different from the metals; first of all, a good quality sample with a high mobility is required to perform the experiment, and a qualified single crystal Bi<sub>2</sub>Te<sub>3</sub> shows the suppression due to the applied field through the whole temperature region, instead of at low temperatures. Single crystal semiconductors, because of the limited amount of defects and impurities, are actually phonon dominant materials. Their temperature dependent electronic transport properties are still not very clear due to our experimental accuracy, *i.e.* the exact power laws. When dealing with their Lorenz ratio, their thermoelectric effect cannot be omitted, *i.e.* the Seebeck coefficient needs to be counted. By considering the Seebeck coefficient along with its experimental error of Bi<sub>2</sub>Te<sub>3</sub> its Lorenz ratio is calculated and we find that it is pretty close to the Sommerfeld value, although there is deviation and becomes large when temperature rises, it is not significant. Due to the study of electronic and phononic transport of single crystal metals and semiconductors, we have better understanding of temperature dependent behaviors of both transports, which may benefit the thermoelectric performance study in the future.

Chapter 4 dealt with the thermoelectric study of nanocomposite Cu<sub>2</sub>Se parent compound and with different dopants. Cu<sub>2</sub>Se is a *p*-type thermoelectric material no matter above room temperature or below room temperature, but with different internal mechanism because Cu<sub>2</sub>Se has different phases at these temperature regimes. From the low temperature electrical resistivity study we find that Cu<sub>2</sub>Se performs a CDW transition even in a hot press (HP) nanocomposite, although the transition is broadened significantly. Different from the structural transition ~130 °C where all the transport properties show discontinuities at the transition temperature, except  $\rho$ , all other quantities such as  $\kappa$ , *S*, and ZT are smooth around the CDW transition temperature, this shows the CDW transition is a weak transition compared to the structural transition. And the CDW transition can be eliminated by Te and Ag doping because these dopants destroy the perfect nesting on the Fermi surface. The fabrication process is also critical to the formation of the CDW transition. By comparing the grain sizes of cold press (CP), CP + annealing, and HP samples, we found that the CDW was significantly suppressed by the smallest grain sizes of the CP sample, but was recovered by the annealing process in which the small grains merged together. Besides, a special oscillation (wave-like fluctuation) of the *dc* I-V curve was observed for Cu<sub>2</sub>Se parent compound and the sample doped with Zn, but the explanation is still not available. From the transport study of Cu<sub>2</sub>Se nanocomposites we found the parent compound has the best TE performance of a ZT value  $\sim 0.14$  at 200 K and higher than the traditional low temperature p-type TE material single crystal bismuth antimony.

Chapter 5 showed our work on the thin films which accommodates the place for the Van der Pauw method. Besides from our researches on nanocomposite bulk TE materials, thin films are quite different. First of all, their properties are highly sensitive to the substrates, and textured film could only be achieved on certain substrate, *e.g.* the bismuth film on a mica substrate. Secondly, their properties are thickness dependent, because for a thin film its thickness is usually on the same order of magnitude or smaller than the grain size in the film, thus when performing the angle dependent transport measurements in an applied field the results are anisotropic. By comparing the similar results of antimony film we conclude that the anisotropic conduction that we observe is a direct result of the large mass anisotropy of the electron effective mass in Bi.

Besides the contexts in the main text, I put our results of  $U(Pd_xPt_{1-x})_3$  in the appendix. Transport properties of pure, 2% and 5% Pd doped single crystal UPt<sub>3</sub> samples are measured, and results reveal that 2% doping doesn't affect much of the properties. This means the carrier concentrations, the band structures keep nearly unchanged, while 5% doping displays an intermediate stage of pure UPt<sub>3</sub> and UPd<sub>3</sub> in electrical resistivity and thermal conductivity, but falls out of the trend in Seebeck coefficient, which becomes a complete *p*-type material up to 300 K. In order to understand the strange behavior of 5% Pd doped UPt<sub>3</sub> in Seebeck coefficient, more experiments need to be done either on the band structure or the phonon spectrum.

### 2. Conclusions

In conclusion, two major projects have been successfully and extensively studied and discussed throughout this dissertation, from which we have better understanding on the thermal and electric conductions in several single crystal metals and semiconductors, and on the thermoelectric properties of copper selenide nanocomposite with different dopants below room temperature. Three instrument setups were built and aimed for an experimental research in the lab, and thus we have the ability to perform electrical resistivity and thermal conductivity measurements on thin films from liquid nitrogen temperature to several hundred Celsius. Future research can be focused on the organic thermoelectric materials, as well as the earth-abundant element TE materials.

# Appendix A: Outlook

In this section I would like to summarize some of my work that is not reflected in the previous chapters, either because they're just some initial work, or they're not quite successful. As the tradition in Opeil's lab, I built (or assembled) at least one equipment (or measuring system), and some of them can be further developed and optimized.

The point-contact spectroscopy (PCS) setup, as mentioned in Chapter 2, was the first setup I tried to build up. There are several kinds of realizations, ours is similar to STM, and is called the poor men's STM. We use the same etched tungsten tip, but the distance between the tip and the sample is smaller than STM, as a result the contact resistance of PCS is around tens of ohms while STM is usually several thousand ohms. Based on this setup design, the most important part is to precisely control the distance, *i.e.* move the tip. We adopt a design using an O-80 screw to move the tip instead of using a piezoelectric crystal. Unfortunately it is not precise enough, and during a whole year debugging the system and excluding other factors, I believe the rough movement of the tip is the core factor preventing me from gathering more meaningful data. The following plots in Fig. A.1 are traditional PCS data of a vanadium sample collected by the

equipment, and I only succeeded once.



Fig. A.1: PCS plots of bias *dc* voltage versus signal detected by the lock-in. (a) Curves of two different contacts at the same temperature; (b) Curves of the same contact at three different temperatures.

The Van der Pauw setup, also introduced in Chapter 2, but this setup hasn't been used to perform thin film measurements yet. When we performed the Bi thin film measurements, I manually changed the configurations from 1 to 2, but the current Van der Pauw setup is able to automatically change the configurations by using a homemade relay switch which can be controlled and programmed through the laptop by LabVIEW. The improved setup has only been tried once and got some results as shown in Fig. 2.17. Further optimizations are needed, especially on the coding part. Also, applying this setup on a real thin film is necessary, rather than on a virtual 4-resistor in Fig. 2.16.

The  $3\omega$  setup is another system needs to be further developed and tested. I think we already finished all preliminary constructions, and it is theoretically correct. The  $3\omega$ setup is a complimentary part of the Van der Pauw setup, and both of them are used to perform measurements on thin films: the  $3\omega$  setup is used to measure thermal conductivity while the Van der Pauw setup is used to measure electrical resistivity. But the  $3\omega$  setup is not limited to use on thin films, it is also able to measure the thermal conductivity of bulk materials, and our tests of this  $3\omega$  setup is to measure the thermal conductivity of a glass (Pyrex) substrate at room temperature. Unfortunately, our trails were both unsuccessful. It looks like the thickness of the sputtering heater is very tricky, and is reflected in the resistance of the heater. Our heaters have resistances one order of magnitude higher than the values in literatures, so that may be the reason of our failure. In the future, the first step is to sputter a thinner heater and succeed in measuring the thermal conductivity of Pyrex substrate, and then extending this method to real thin films is meaningful.

Besides the instrument-based projects mentioned above, there is another unsuccessful MoSSe project which is not mentioned both in the main text and also the appendix. MoSSe is one specimen of the MoS<sub>x</sub>Se<sub>2-x</sub>, and all of them are semiconductors and may have good TE properties according to the theory. M. K. Agarwal et al. were able to grow MoS<sub>x</sub>Se<sub>2-x</sub> ( $0 \le x \le 2$ ) single crystals by the direct vapor transport technique to the maximum size of 15 mm by 10 mm by 0.3 mm in 1980's, and it was very sensitive to the furnace. We tried to setup a similar circumstance with our one-zone furnace, but finally we were not able to achieve the single crystal, instead we got powders. From XRD, shown in Fig. A.2, we believe MoSSe is successfully synthesized, however, these powders are thermoelectrically useless because no matter the specimens were CP or HP, all of them had huge resistance ( $k\Omega - M\Omega$ ). According to the literature their resistivity should on the order of several  $\Omega$ -cm, *i.e.* the resistance of the as-fabricated sample is tens

of ohms. The materials do not have a liquid phase, so it is not possible to melt them and form a solid ingot, we tried but we still got powders. So it looks like the fabrication process is critical, one must strictly follow the steps shown in the literature to grow the crystals, especially providing the needed two-zone furnace.



Fig. A.2: (a) XRD patterns of MoSSe powders. There is also one MoSe<sub>2</sub> XRD pattern, because MoSSe and MoSe<sub>2</sub> have the same crystal structure, so their patterns are very similar, only the peaks shift a little bit. (b) Temperature gradient in the horizontal one-zone furnace, it was used as a two-zone furnace when fabricating MoSSe.

Besides the above contents excluded from the main text and the appendix, there are still possible improvements to my already finished two projects, *i.e.* the Lorenz project and the  $Cu_2Se$  project. For the Lorenz project, we have done extensively magneto-thermal-resistance measurements on single crystal metals and semiconductors, and for these single crystals, it is possible to perform first-principles calculations which is very hard for nanocomposites. With the provided experimental results, one is able to find out how well the theory coincides with the experiments. For the Cu<sub>2</sub>Se project, all of our samples are nanocomposites, in order to find out the internal physics mechanism the best specimen candidate is always single crystals, but due to the low vapor pressure of Se it is very hard to grow Cu<sub>2</sub>Se single crystals. Although for the single crystals, their TE performance may not be as good as nanocomposites, it benefits the study on the dc I-V curve oscillations and relevant CDW transition, such as Shapiro steps when applying an rf-frequency ac signal or sliding CDW through a pulsed electric field.

Generally speaking, the improvement of TE performance during this decade is mainly due to the introduction of nanostructuring into the fabrication processes; however, it looks like this approach comes to its limit and is very hard to use this trick to further improve the figure of merit. As a result, researches began to consider other categories of materials, such as the organic thermoelectric materials, which became very popular recently. Besides, researchers also tried to use earth abundant elements to build thermoelectric unit, which could reduce the price of TE devices significantly. In order to make TE devices more popular in practice, safe TE materials without toxic elements are needed and they are also a direction for the current researchers.

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# Appendix B: Transport in the normal phase of $U(Pt_{1-x}Pd_x)_3$ with x = 0%, 2% & 5%

## 1. Introduction

UPt<sub>3</sub> is the first found heavy-fermion compound superconductor, which has a critical temperature of  $T_{\rm C} = 0.5$  K and an anti-ferromagnetic transition at  $T_{\rm N} = 5$  K [1,2]. The specific heat data above transition temperature  $T_{\rm C}$ , which could be fit by the law  $C_v = \gamma T + \beta T^3 + \delta T^3 \log \left( \frac{T}{T_{SF}} \right)$ , show a pretty large  $\gamma = 440 \text{ mJ}/_{K^2 \text{ mol}}$  U and a strong spin-fluctuation phenomena from the logarithmic term in the normal Fermi liquid state [1,3,4]. People have already done a lot of transport measurements on the normal state of UPt<sub>3</sub>, however, very few results were reported on Pd doped UPt<sub>3</sub>, which were found to have a crossover from anomalous to conventional antiferromagnetism at a certain doping level [5]. In this short paper, we report our transport results on high quality single crystal U(Pt<sub>1-x</sub>Pd<sub>x</sub>)<sub>3</sub> with different doping of 0%, 2% and 5% from 5 K to 300 K. We compare our pure UPt<sub>3</sub> data with Framse *et al.*'s data [6], and they're in good accordance, especially the Seebeck results, while ours has lower electrical and thermal conductivities. The UPd<sub>3</sub> data are adopted from Zaplinski *et al.*'s work [7].

## 2. Transport Properties

The traditional dimensions of 3 single crystals are 1 mm by 2 mm by 8 mm, and all of the transport properties are measured along the a-axis. Samples are soldered on 2 pieces of gold plated copper disks, and measured by the Physical Properties Measurement System (PPMS) from Quantum Design (QD) using a thermal transport option (TTO) with a 2-probe method. We also performed transverse measurements in 9 T field, but very few distinctions could be observed, so only zero field results are reported here.

Fig. B.1 shows the electrical resistivity data of different doping. Basically, all Pd doped UPt<sub>3</sub> samples behave similar to pure UPt<sub>3</sub> single crystals, but high Pd doping significantly decreases the resistivity, as UPd<sub>3</sub> itself has a lower resistivity than UPt<sub>3</sub>. We also notice that although  $U(Pt_{1-x}Pd_x)_3$  is a heavy-fermion compound, however, the resistivity nonlinearly and monotonically decreases as temperature decreases but without a common peak observed in a lot of other heavy-fermion compounds. This is a feature due to the single-impurity Kondo effect [1].



Fig. B.1: Electrical resistivity vs. temperature.



Fig. B.2: Thermal conductivity vs. temperature.

Fig. B.2 shows the temperature dependent thermal conductivity of different Pd doping, and they also follow the similar trend as electrical resistivity with respect to the doping. The single crystal UPd<sub>3</sub> has the highest thermal conductivity results while UPt<sub>3</sub> is at the bottom; 5% and 2% Pd doped UPt<sub>3</sub> are in between them. However, although Pd and Pt have the same valence electrons, the thermal conductivity data of  $UPt_3$  seem to have saturation at higher temperatures. The curves raise their heads around 300 K with increasing Pd towards to the pure UPd<sub>3</sub> end. It is also worth noticing the linear temperature dependence of thermal conductivity of these single crystals below 30 K and above 200 K. The electronic part of thermal conductivity can be extracted by assuming the validity of the Wiedemann-Franz law, *i.e.*  $\kappa = LT/\rho$ . Fig. B.3 shows the temperature dependence of the dimensionless Lorenz number, which is defined as  $L/L_0$  where  $L_0 = 2.443 \times 10^{-8} \text{ V}^2/\text{K}^2$  is the Sommerfeld value. Basically, all of the curves approach unity as temperature towards 0, while at higher temperatures the Lorenz number increases sharply and comes to a maximum around  $T_{\text{max}} \sim 24$  K for all of them, and then slowly go down to some definite value which is different for different doping. In strong correlated systems such as heavy-fermion compounds, due to the small electron mean free path, phonons can dominate the heat transport and result in a Lorenz number several times of the Sommerfeld value  $L_0$  [6]. The lattice thermal conductivity usually has a peak occurring at a temperature about 10% of the Debye temperature  $\Theta_D$  [8], and results in a peak in the dimensionless Lorenz number  $L/L_0$ . The Debye temperature of pure single crystal UPt<sub>3</sub> is 217 K deduced from sound velocity measurements [1,9], and our peaks at around 24 K are very close to 0.1  $\Theta_D$ . Since  $L = L_e(1 + \kappa_{ph}/\kappa_e)$  where  $L_e = \kappa_e \rho/T = L_0$  by the Wiedemann-Franz law, the lattice thermal conductivity of 5% Pd doped UPt<sub>3</sub> is significantly suppressed at  $T_{max}$  while 2% one is little affected.



Fig. B.3: The experimentally determined value of dimensionless Lorenz ratio from the Wiedemann-Franz law.



Fig. B.4: Seebeck coefficient vs. temperature.

Seebeck coefficients are measured up to 300 K and shown in Fig. B.4. According to the literature, the pure single crystal UPt<sub>3</sub> has a pronounced positive peak at around 8 K in its Seebeck curve [6], which nearly coincides with the maximum in the temperature derivative of the electrical resistivity and is an estimate of the spin-fluctuation temperature [10]. Actually in our data we indeed observe a sharp increase of the Seebeck coefficient at low temperature; however, our data could not show the decrease at lower temperatures due to our equipment limitations. The 2% Pd doped sample behaves very similar to the parent compound and looks like to have a peak below 10 K. Both 0% and 2% Pd doped UPt<sub>3</sub> sample change their sign of Seebeck coefficient at 21 K and 14 K, respectively; and reach nearly constant values of -10.5  $\mu$ V/K and -11  $\mu$ V/K above 100 K, respectively, where their electrical resistivity are going to saturate. The 5% doped sample is the most unexpected one, whose Seebeck has a quite strange temperature dependent behavior: it is always positive (*p*-type) rather than changing its sign at some certain temperature within our temperature range, and by considering that all the Seebeck coefficient goes to zero when the temperature approaches zero, so it is unlikely that the Seebeck could change its sign below 10 K and then turn back to zero. However, we can still observe a positive but not pronounced peak at 14 K, without a monotonic trend above 50 K: the Seebeck coefficient goes to a local minimum at 50 K

and then increases its value with a maximum at 180 K and then decreases again without a saturation value within 300 K. On the other side, pure UPd<sub>3</sub> behaves a quite different temperature Seebeck curve, which decreases linearly like a *p*-type metal and changes sign at 100 K, which is much higher than UPt<sub>3</sub>. To the contrary, 5% Pd doped UPt<sub>3</sub> doesn't fall in between pure UPt<sub>3</sub> and UPd<sub>3</sub>, and behaves neither saturated nor linear-like above 100K, which could be probably due to a rather complicated replacement of Pt atoms by Pd atoms, and with strong interactions between these two sets of atoms, and results in a Seebeck differ from both pure parent compounds. Although we can simply regard 5% doped sample as a superposition of majority pure UPt<sub>3</sub> and minority UPd<sub>3</sub>, which have opposite Seebeck coefficients, however, it seems at all temperature range the *p*-type carriers, or the holes, dominate the contribution to the Seebeck effect. Finally a positive Seebeck coefficient is observed, but the detail mechanism is still unclear.

## 3. Conclusions

Transport properties of pure, 2% and 5% Pd doped single crystal UPt<sub>3</sub> samples are measured, and results reveal that 2% doping doesn't affect much of the properties, which means the carrier concentrations, the band structures remain nearly unchanged, while 5% doping displays an intermediate stage of pure UPt<sub>3</sub> and UPd<sub>3</sub> in electrical resistivity and thermal conductivity, but falls out of the trend in Seebeck coefficient, which becomes a complete *p*-type material up to 300 K. In order to understand the strange behavior of 5% Pd doped UPt<sub>3</sub> in Seebeck coefficient, more experiments need to be done either on the band structure or the phonon spectrum.

### References – Appendix B

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# Appendix C: Publications and Manuscripts

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- [11] Transport in the Normal Phase of  $U(Pt_{1-x}Pd_x)_3$  with x = 0%, 2% & 5%, Mengliang Yao, and Cyril Opeil, unpublished (Appendix B).