Chapter 6

Transport in Ag₃Se

This chapter is principally about the thermoelectric performance of Ag₃Se near its phase transition. In the sample studied here the Hall carrier concentration does not differ measurably in the order and disordered phases; this fact considerably simplifies arguments based on band structure analysis. While many samples show similar behavior, other samples show a sharp increase in $n_H$ in the disordered phase; the reason for this distinction remains unclear. Without any measured difference in band structure, the Seebeck and $zT$ are enhanced in the ordered phase compared to the disordered.

This increase in $zT$ is not easily explained using standard band-structure analysis (e.g., BoltzTraP [127]). In this chapter I will introduce super-ionics as thermoelectric materials and explain why they are of interest. Then I will provide a brief overview of the band structure modeling used for this thesis. After this I will present and analyze the transport data of Ag₃Se and argue that the difference in its properties above and below its phase transition are not easily explained by band structure modeling.

In the final chapter, after I have also presented the transport of Cu₂Se, I will develop an explanation for its physics on the basis of the phenomenology of order-disorder transitions [95] and Onsagers phenomenology of non-equilibrium thermodynamics [132]. I will suggest that these effects may occur broadly; it may be that the sudden transformation of the phase transition brings a more general effect into contrast.
6.1 Ion conducting thermoelectrics

Mixed ion-electron conductors (MIECs) are of recent and increased interest as thermoelectric materials [1, 199, 50, 133, 200, 206, 121, 30, 179, 185, 66, 45]. MIECs are materials that conduct both ions and electrons [167]. This is of course a very broad category that includes semiconductors and solid electrolytes. They can be subcategorized by the relative size of ionic conductivity ($\sigma_i$) and electronic conductivity ($\sigma_e$) with the physics varying substantially from the $\sigma_i \gg \sigma_e$ regime to the $\sigma_e \gg \sigma_i$ regime. In some materials such as solid oxides used in fuel cells, these regimes may be bridged in a single material under varying conditions of oxygen partial pressure and temperature.

Thermoelectric ion conductors operate entirely in the $\sigma_e \gg \sigma_i$ regime. This regime is inescapable unless an entirely new conception of what makes a good thermoelectric material is made as compared to what is studied now. A good thermoelectric is a heavily doped semi-conductor with a carrier concentration generally optimized at between $10^{18}$ cm$^{-3}$ and $10^{21}$ cm$^{-3}$ [180], and an electrical conductivity in the $10^4$ S/m to $10^6$ S/m regime in which the electronic ($\kappa_e$) and lattice ($\kappa_L$) portion of thermal conductivity are nearly the same. Super-ionics are by their phenomenological definition the best ionic conductors. They have ion conductivities that are similar to that of a liquid, $\approx 10^2$ S/m. Therefore even in the most extreme conceivable case an ion-conducting thermoelectric has $\sigma_i$ less than 5% of $\sigma_e$.

Direct enhancement of thermoelectric material conductivity by adding ionic conduction is therefore impossible. Fortunately, this simplifies the measurement procedure for total thermal and electrical conductivity; the great care must be taken in making DC measurements of materials with two species with order of magnitude different diffusion timescales [167, 164, 165] can here be ignored. The principal consideration is that the electrodes are blocking to ions so that the ion conducting specie does not leave the material. Empirically the graphite blocker layer between thermocouple and electrode accomplished this purpose. When that layer was forgotten or broken through, the Niobium thermocouple wire used for the electrode developed a
fine metallic coating and was rendered useless.

The driver of recent interest in MIEC thermoelectrics has been their extremely low thermal conductivity. A principal problem of engineering good thermoelectric material is to find methods for scattering lattice vibrations (phonons) and thereby reduce $\kappa_L$ without also scattering electrons and thereby reducing $\sigma$. In $\text{Ag}_2\text{Se}_{0.05}\text{Te}_{0.05}$ $\kappa_L$ is only 0.5 W/mK at 400 K [50] and $\text{Ag}_8\text{GeTe}_6$ has been reported as having a glass-like thermal conductivity of 0.25 W/mK at 300 K with only negligible contribution from electrons. Though these noble metal chalcogenides are the subject of this thesis and in fact have a longer history as thermoelectric materials than is commonly appreciated [24], the driver of the recent interest in MIECs has been $\beta - \text{Zn4Sb3}$.

In 1997 Caillat et al. first synthesized $\beta - \text{Zn4Sb3}$ as a thermoelectric material [30]. They determined it to have a maximum $zT$ of 1.3 at 670 K which at the time was the highest ever measured at that temperature. This was driven by a $\kappa_L$ at or slightly above $0.65\text{Wm}^{-1}\text{K}^{-1}$ from 400K to 650K. They determined this to be very close to the thermal conductivity of a glass in accordance with Cahill’s formalism [28, 29]. On the basis of crystallography Snyder et al. [179] suggested that this low $\kappa_L$ was due to scattering off of disordered interstitials.

Density functional theory analysis by Toberer et al. [186] showed that the Zn interstitial sites were of almost identical energy to the ground state sites, with meta-stable pathways connecting them. Both a nearly isoenergetic interstitial site and meta-stable energetic pathways are considered necessary conditions for super-ionic conduction [87]. Tracer diffusion experiments confirmed $\text{Zn}_4\text{Sb}_3$ to have a liquid-like ion diffusivity with site hopping activation energy only 20% higher than that of $\text{AgI}$ [35]. $\text{Zn}_4\text{Sb}_3$ is therefore a super-ionic thermoelectric material [21, 151].

Super-ionic materials are often written about as having a molten sub-lattice of conducting ions [22, 103]. As this analogy was coined in reference to the liquid-like diffusivity of the conducting ion ($10^{-5}\text{cm}^2/\text{s}$) and the enthalpy of formation comparable to that of their melt, [21, 22] care must be taken in extending it beyond its physical underpinnings. It has been suggested in two ways that the lattice thermal conductivity may have properties similar to that of a liquid: that they should show
phonon softening due to coherent oscillations like a liquid [6], and that their constant volume heat capacity ($c_V$) should decrease with increasing temperature like a liquid [122, 189, 17].

The liquid-like heat capacity was proposed by Liu et al. in order to explain a decrease in $c_P$ they observed above 800K in Cu$_2$Se [122]. While a solid has $c_V = 3k_b$, a liquid only has $c_V = 2k_b$ [189]. The solid heat capacity is due to the kinetic and potential energy contributions to heat capacity by the equipartition theorem. As in a mono-atomic gas, there are three degrees of freedom for position and momentum each and so $c_v$ of a solid is $6 \times k_b/2 = 3k_b$. In a crystalline solid these contributions are split between two longitudinal and one transverse (or shear) propagation modes. A liquid is incapable of propagating all transverse oscillations and therefore loses the heat capacity associated with the potential energy of those modes (up to $k_b$).

In real liquids $c_V$ is observed to decrease with temperature. Bolmatov et al. compiled data for twenty-one liquids showing this trend [17]. As an example, their data for Pb is shown in Figure 6.1. They model this trend as being due to two characteristic frequency. The first is the characteristic frequency of lattice oscillations, the Debye frequency ($\Omega_D$). The second is the characteristic frequency of liquid hopping, which they call the Frenkel frequency ($\omega_F$). Only shear modes with characteristic frequency ($\omega < \omega_F$) disappear. In this frequency regime the liquid atoms move fast enough to

Figure 6.1: Heat capacity of liquid lead and rubidium with fit to theory. As temperature increases low frequency transverse modes disappear and thereby reduce $c_V$. Figure from Bolmatov et al. (2012) [17].
Figure 6.2: The fluctuations of ions between interstitial sites causes phonon mode to soften and scatter. In Zn$_4$Sb$_3$ Schwelka et al. [173] observed a strong anharmonic ratting of an Sb-dimer that they found could explain its anomalously low thermal conductivity. This behavior was found to effect the heat capacity even in the ordered phase, as evidenced by an Einstein peak in the heat capacity. If this behavior is a more general attribute of super-ionic materials in both their ordered and disordered phases, it may cause their low thermal conductivity. In his studies on single crystal Cu$_{1.8}$Se Danilkin found substantial mode softening in Cu$_{1.8}$Se [44].
damp out the oscillation. Above this frequency the liquid atoms move slow compared to the perturbation and so appear as a solid. As temperature increases more lattice vibration modes and ion hopping modes contribute to this behavior, with their contribution determined by the characteristic quantity. At $k_b T \gg \hbar \omega_D, \hbar \Omega_F$, the heat capacity simplifies to:

$$c_v = k_b \left( 3 - \left( \frac{\omega_F}{\omega_D} \right)^3 \right)$$

(6.1)

From inelastic neutron scattering measurements, the Frenkel timescale of Cu$_2$Se is 1 picosecond at 430K [42]. This corresponds to a $c_v = 2.98 k_b$. Though this casts doubts on the explanation of Liu et al. [122], this author is unaware of any experiments showing the ion hop time of Cu$_2$Se at high temperature. One should also not discount the possibility that another material may show liquid-like reduction in its heat capacity much more strongly than Cu$_2$Se does.

While the liquid-like fluctuations of ions may not eliminate phonon propagation modes, they may scatter them. Ultra-sonic attenuation is a common feature of many solid electrolytes [3]. The theoretical explanations of Aniya for this behavior treats the mobile ions as a liquid free to move through out the lattice and thereby collide with the mobile cores [6]. A treatment of this class of materials that ignores the significant portion of ion life-time spent between interstitial sites [87] may not be able to fully capture their behavior.

### 6.2 Band Structure Modeling

In order to understand how Ag$_2$Se may have enhanced thermoelectric performance as compared to predictions based on its band structure, a brief overview of the relationship between band structure and Seebeck coefficient is necessary.

The electronic transport properties of heavily doped thermoelectrics can be typically described by modeling their electronic band structures [180, 127]. If the full electronic band structure is known — or more realistically predicted by density func-
Figure 6.3: Left: Example of a single parabolic band. The band shown is a valence band as for a p-type conductor. The effective mass \( m^* \) determines the curvature of the band. The carrier concentration is the number of carriers between the band edge and the Fermi level.

Right: Example \( \alpha \) versus \( n_H \) or Pisarenko plot. As \( m^* \) increases at constant \( n_H \), \( \alpha \) increases.

Theoretical — then the transport coefficients could be computationally determined (e.g., by BoltzTRaP [127]). However, simplified models that take into account only part of the band structure are extremely successful at predicting transport properties [154]. These models are successful because only band states within \( 3k_B T \) of the electron chemical potential (i.e., the Fermi level) contribute significantly to electron transport [128]. The starting point for these models is the single parabolic band [170].

Thermoelectrics are heavily but not metallically doped, so that the band of the dominant conductor tends to dominate, but the Fermi level is not far from the band edge. A single parabolic band (SPB) has a dispersion relationship of form:

\[
E = \frac{\hbar^2 (k - k_0)^2}{2m^*}
\]  

(6.2)

This structure is shown in Figure 6.3(a). The effective mass \( m^* \) is typically given in units of electron masses \( m_e \). A heavier band (large \( m^* \)) has a low rate of curvature.
of $E$ with respect to $k$; increasing $k$ increases $E$ only slightly. In a light band (small $m^*$) increasing $k$ increases $E$ significantly.

If $m^*$ and the band chemical potential ($\mu$) are known, than the carrier concentration may be written as:

$$n = 4\pi \left( \frac{2m^* k_b T}{\hbar^2} \right)^{3/2} F_{1/2}(\eta),$$

in which $\hbar$ is Plancks constant, $\eta = \frac{\mu}{k_b T}$ is the reduced chemical potential and $F_j(\eta)$ is the Fermi integral of order $j$.

If the energy dependence of scattering ($\lambda$) is also known, than transport variables may be modeled as well. In the case of scattering by acoustic phonons $\lambda = 0$. This is a good assumption for thermoelectric materials above the Debye temperature. In this model the Seebeck coefficient may be expressed as:

$$\alpha = \frac{k_b}{e} \left( \frac{(2 + \lambda) F_{\lambda+1}}{(1 + \lambda) F_\lambda} - \eta \right)$$

(6.4)

The general behavior can be understood well if the degenerate (e.g., metallic) limit of Equation 6.4 is taken.

$$\alpha = \frac{\pi^{8/3} k_b^2}{3q\hbar^2} n^{-2/3} T m^* (1 + \lambda)$$

(6.5)

The inverse dependence of Seebeck on $n$ argued for generally in the introduction is again present. Notably increased $m^*$ results in increased Seebeck coefficient. This can be explained by a two step argument. A heavy band will have a lower $\eta$ for the same $n$ compared with a light band. A lower $\eta$ results in a larger Seebeck coefficient by equation 6.4. This effect is depicted in Figure 6.3(a) by means of a Pisarenko ($\alpha$ versus $n$ or $n_H$) plot.
6.3 Prior Work on Ag\textsubscript{2}Se

As established in Chapter 5, Ag\textsubscript{2}Se shows a first order transition at 408 K as seen in both crystallography and calorimetry. Electronically, Ag\textsubscript{2}Se is a n-type material with high electron mobility and low thermal conductivity. These two attributes in combination give it promise as a high $zT$ material near room temperature [1], but with two principal problems. The first is carrier concentration control, for which there is some uncontrolled effect in synthesis. The sample I will discuss below showed no carrier concentration shift through its phase transition, but many of the samples show a significant shift at that temperature [46]. The Seebeck coefficient of a second sample, produced by a different laboratory, shows the same trend as the sample principally studied here.

The second problem is hysteresis observed in transport properties in the low temperature phase and near the phase transition temperature [2]. These effects may be due to the kinetics of microstructural reorganization, as they appear in multiple materials. One example of this is Ag\textsubscript{2}Se\textsubscript{0.5}Te\textsubscript{0.5} [50]; other materials showed this effect but these instabilities rendered writing a meaningful publication on their thermoelectric performance impossible. In his paper on Ag\textsubscript{2}Se my colleague Tristan Day applied band structure modeling to estimate the effective mass of the low temperature phase $0.2m_e$ and that of the high temperature phase to $0.3m_e$ [46].

6.4 Transport Measurements

Electrical conductivity (Figure 6.4(b)) was measured in the Van der Pauw geometry (see Chapter 2). Substantial hysteresis was observed both in the phase transition temperature and in the data in the low temperature phase. The data above the phase transition temperature is consistent on heating and on cooling. Though the data values on heating and cooling are inconsistent, the shape of the curves shows the same general trend. Above room temperature the conductivity linearly increases with temperature and then flattens out before the phase transition temperature. The
conductivity drops by a factor of two at the phase transition temperature.

The Seebeck coefficient (Figure 6.4(a)) was measured by the ramp method discussed in Chapter 3 at 10 Kelvin per minute. It shows a similar behavior to the conductivity. At the temperatures at which the electrical conductivity increases, the Seebeck decreases. At the temperatures at which the electrical conductivity flattens, the Seebeck coefficient flattens. At the phase transitions it decreases slightly. During the phase transition the voltage versus ∆T data could not be fit to a line and so is not shown. The phase transition occurs at 405 K on heating and on 390 K on cooling. This hysteresis is expected for a first order phase transition. A second sample produced in a different lab by Dr. Fivos Drymiotis was measured by the oscillation method and showed a comparable change in the Seebeck coefficient through the phase transition.

The thermal diffusivity (figure 6.5(a)) also shows a hysteresis in its phase transition temperature. The thermal diffusivity shows far less consistent behavior on heating and cooling than the electrical properties. In the high temperature phase there is a 10% discrepancy between the heating and cooling data. The phase transition range is extended on cooling over a 15 K range. The low temperature data shows a more significant discrepancy between the heating and cooling data.
Figure 6.5: Thermal diffusivity (a) and Calorimetry data (b) for Ag$_2$Se measured on both heating and cooling.

In the context of identification of the order of the phase transition, the calorimetry was also discussed in Chapter 5.2 As Ag$_2$Se has a first order phase transition, the peak in its calorimetry at 410 K represents an enthalpy of formation. At temperatures further below 400 K and above 420 K it is an accurate measurement of the heat capacity, and is used to calculate $\kappa$ and $zT$. Between 400 K and 420 K the heat capacity used is that measured at 400 K — 0.317 J/gK.

Figure 6.6: Hall Carrier Concentration (a) and Hall Mobility (b) for Ag$_2$Se measured on both heating and cooling.
The Hall coefficient was measured concurrently with the electrical conductivity via the Van der Pauw method at 2 Tesla. The Hall carrier concentration (Figure 6.6(a)) and Hall mobility (Figure 6.6(b)) were thereby determined on heating and cooling. The Hall carrier concentration of Ag$_2$Se varies smoothly through the phase transition. This suggests that the band curvature (i.e., effective mass) and the doping level are not altered measurably by the structural changes of the phase transition. The Hall mobility decreases by 50% through the phase transition. This is consistent with a sudden increase in the ion disorder and conductivity leading to increased scattering of electrons. It also explains the decrease in electrical conductivity observed at the phase transition temperature. Pardee and Mahan suggested that a steady Arrhenius increase in ion conductivity is observed due to Frenkel defect formation in both type I and type II super-ionics [151]. Such defect formation in Ag$_2$Se may alter the carrier concentration by localizing electrons more or less than the ground state sites. This would be indicated by a difference in Ag ion effective valency.

Below 360 K, the cooling Hall carrier concentration increases steadily with temperature; over the same range Seebeck decreases steadily. As the Hall carrier concentration become constant, so does the Seebeck coefficient. The data was of insufficient quality to prove this connection as causal. The Seebeck coefficient shows a 15% decrease from the low temperature to the high temperature phase, despite no measured shift in the carrier concentration. This data is inconsistent with the band model advanced in equation 6.5.

The total thermal conductivity of Ag$_2$Se is decreased by a factor of two in the disordered high temperature phase as compared to the ordered low temperature phase, see Figure 6.7(a). The Lorenz number of $L = 1.8 \times 10^{-8}$ WΩK$^{-2}$ was used to calculate the electronic portion of the thermal conductivity. This quantity is taken from Day et al.’s [46] single parabolic band model of data from their samples and literature samples. From this Lorenz number $\kappa_e$ and $\kappa_L$ may be calculated. The lattice thermal conductivity of Ag$_2$Se decreases only slightly as the temperature increases through the phase transition temperature, indicating that the majority of the change in total thermal conductivity is due to the decrease in electrical conductivity, see Figure 6.7(a).
Figure 6.7: Left: Measured total and modeled lattice thermal conductivity of Ag$_2$Se. Right: $zT$ of Ag$_2$Se. The $zT$ in the ordered phase is markedly higher than the $zT$ in the disordered phase.

The resulting lattice thermal conductivity is 0.35 W/mK below the phase transition temperature and 0.25 W/mK above it. This indicates that the Lorenz number of Day et al is correct.

From the transport data presented above, the $zT$ of Ag$_2$Se was determined on both heating and cooling, see Figure 6.7(b) Where necessary corrections to the temperature were made to align the phase transitions of all transport properties. In the calculated range between 320 K and 420 K $zT$ is bound between 0.3 and 0.4, and it decreased upon transition to the disordered phase. The decrease in $zT$ is 30%, which is consistent with the anomalous 15% decrease in the Seebeck coefficient at the phase transition temperature as $zT$ varies with Seebeck squared. What explains this anomalous enhancement in Seebeck and $zT$?

One possible explanation would be a decrease in $m^*$ from the ordered to the disordered phase. By equation 6.5 decreasing $m^*$ should result in a decreased Seebeck coefficient. However, the band structure model of Day et al. suggests a moderate increase in $m^*$ from the ordered to the disordered phase, see Figure 6.8(b). Such an increase is not compatible with the observed decrease in Seebeck coefficient. Day et al suggest that the increase is from 0.2$m_e$ to 0.3$m_e$, but the error bars on their fit are
Figure 6.8: The ratio (a) of $\kappa_E$ to $\kappa$ is nearly identical on either side of the phase transition. Pisarenko plot (b) for Ag$_2$Se. The disorder phase has a slightly larger $m^*$ than the ordered phase. Modified version of Figure 2a in Day et al. [46] Courtesy of Tristan Day

such that the increase may be much smaller even than that.

Thermoelectric performance can also improve a more favorable portion of thermal transport due to electrons rather than the lattice; this is certainly possible given the decrease in $\kappa_L$ observed, see Figure 6.7(a). The formula for $zT = \sigma\alpha^2/\kappa T$ can be reformulated in terms of $L$ and $\kappa_e$ as:

$$zT = \frac{\alpha^2 \kappa_e}{L \kappa}$$

(6.6)

With the contribution due to $\alpha$ discussed above and $L$ varying significantly only for large changes in the Fermi level, the remaining contribution can be expressed as $\frac{\alpha^2 \kappa_e}{\kappa}$. This term varies by less than 5% through the phase transition temperature, see Figure 6.8(a). This indicates that the enhancement in $zT$ is entirely due to the enhancement in $\alpha$ noted above.

The enhancement in $zT$ and $\alpha$ requires an alternate explanation from the single parabolic band model. More complex band effects such as band convergence [153] or resonant impurities [77] might be considered to explain the behavior. However,
these features are inconsistent with the constant $n_H$ observed and the near constant $m^*$ [154]. This suggests that an alternate explanation for the Seebeck and $zT$ enhancement is required. This explanation must in some way be beyond that which even complex band structure modeling can capture. Over the next two chapters I will develop that explanation: co-transport of entropy associated with the order process leads to enhanced Seebeck and $zT$. 