Chapter 8

Order and Ion Enhanced Thermoelectrics

In Chapter 6 I presented data showing that the ordered phase of Ag_2Se has a larger zT in its ordered phase than its disordered phase, see Figure 8.1(a). This zT enhancement was predicted to within 5% by a corresponding enhancement of Seebeck, see Figure 8.1(b). The Seebeck change was shown to be neither predicted by the effective mass determined by Day *et al.* [46] or the measured Hall carrier concentration through the phase trasnsition.

In Chapter 7 I presented data showing that just below Cu_2Se and $Cu_{1.97}Ag_{0.03}Se$'s phase transition an enhancement in their zTs of 100% or more was observed, see Figure 8.1(c). This enhancement seemed driven by an 80% increase in their Seebecks over a 60 K temperature range, see Figure 8.1(d). In Cu_2Se n_H and μ_H could be measured through the phase transition in temperature. It was shown that the variation in n_H explained half of the peak in Seebeck, and that the temperature profile of the remaining part of the Seebeck peak explained the peak in zT. Bipolar conduction made a similar analysis of $Cu_{1.97}Ag_{0.03}Se$ impractical.

In this chapter I will provide an explanation for this enhancement in thermoelectric performance. First, I will explain based on the Onsager equations how there might be additional Seebeck and zT beyond that predicted by band structure modeling. Second, I will show that the differing behaviors of Ag_2Se and Cu_2Se can be explained by the Landau theory of order-disorder phase transitions. Finally, I will present

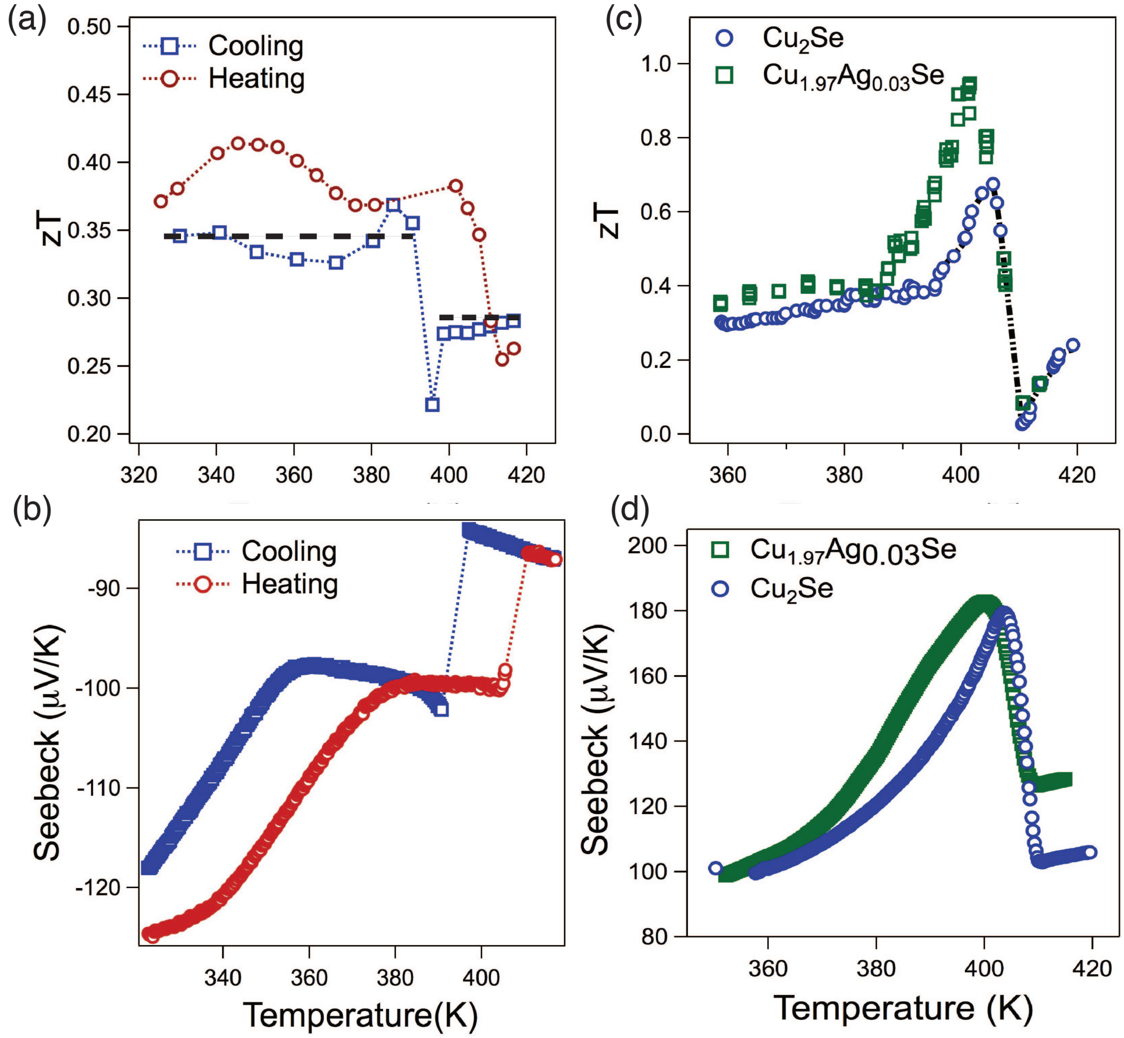

Figure 8.1: Key results of this thesis. Concurrent with its first order transition there is a step change in Ag_2Ses zT (a) and Seebeck (c). The second order transition of Cu_2Se results in a sharply peaked zT (a) and Seebeck (d). The zT and Seebeck of the mixed phase transition of $Cu_{1.97}Ag_{0.03}Se$ resembles that of its Cu_2Se main phase. Dotted lines are guides for the eye.

in detail a similar analysis on the basis of the ionic nature of the particular order-disorder phase transitions. This will allow me to present particular literature results supportive of my hypothesis and provide an experimentally tractable basis for testing these theories.

8.1 Ordering Entropy Enhancement

In Chapter 7 I presented the Onsager coefficients typically presented [69] for a thermoelectric system. It was on the basis of a two term entropy production equation of form:

$$T\dot{S} = -J_s \cdot \nabla T - J_e \cdot \nabla \mu_e \tag{8.1}$$

In which $V \equiv \frac{\tilde{\mu_e}}{e}$ and J_e is a quantity flux rather than a charge flux, *i.e.* defined by $J = qJ_e$. This leads an Onsager matrix of form:

$$\begin{bmatrix} J_e \\ J_s \end{bmatrix} = - \begin{bmatrix} {}^2L_{ee} & {}^2L_{es} \\ {}^2L_{se} & {}^2L_{ss} \end{bmatrix} \begin{bmatrix} \nabla\tilde{\mu_e} \\ \nabla T \end{bmatrix} \tag{8.2}$$

In which the subscript 2 is used for didactic purposes. But imagine if there is a second thermodynamic quantity that transports. Without loss of generality, lets call it m and lets call its conjugate flux h. Then the corresponding internal energy differential to that used for Equation 8.2 is:

$$du = Tds + \tilde{\mu_e}dn_e + hdm \tag{8.3}$$

The corresponding entropy production is:

$$T\dot{S} = -J_s \cdot \nabla T - J_e \cdot \nabla \mu_e - J_m \nabla h \tag{8.4}$$

As a sidenote, if $J_m > 0$ than Equation 8.4 will apparently not capture the entirety of the entropy transported, though this problem can be overcome if J_s is replaced with some other entropy-like flux [132]. In this case there would be dissipation from a non-electronic transport quantity that must affect the maximal zT and η of the system. In the analysis below I principally consider the condition of $J_m = 0$, and so this complication does not enter in.

The Onsager matrix that corresponds to Equation 8.4 is:

$$\begin{bmatrix} J_e \\ J_m \\ J_s \end{bmatrix} = - \begin{bmatrix} {}^3L_{ee} & {}^3L_{ms} & {}^3L_{es} \\ {}^3L_{me} & {}^3L_{mm} & {}^3L_{ms} \\ {}^3L_{se} & {}^3L_{sm} & {}^3L_{ss} \end{bmatrix} \begin{bmatrix} \nabla\tilde{\mu}_e \\ \nabla h \\ \nabla T \end{bmatrix} \tag{8.5}$$

The essential complication arises from this: ${}^2L_{se} \neq^3 L_{se}$ for all conditions, but ${}^3L_{se}$ is that which is calculated by the band structure models presented earlier and generally calculated from density functional theory. The discrepancy between them gives the contribution of entropy co-transport to thermoelectric performance. This is not to say that the kinetic theory that underlies such calculations is incorrect, but rather that if incomplete information is given to them they cannot provide the correct results. The measure Seebeck coefficient is always give by:

$$\alpha = \frac{\nabla V}{\nabla T}_{J_e=0} = \frac{1}{q}\frac{-{}^2L_{se}}{{}^2L_{ee}} \tag{8.6}$$

With $J_e = 0$ indicating the material is measured with an open electrical circuit. The relation between the Onsager L coefficients from Equation (8.1) and those from Equation (8.4) will depend on the boundary conditions, *i.e.* $\nabla h = 0$ or $\nabla m = 0$. The cases of both ∇h, $\nabla\tilde{\mu}_e = 0$ and $J_m = 0$, $J_e = 0$ were both considered by DeGroot in the context of thermodfifusion [132], while the case of $J_e = 0$, $\nabla m = 0$ was recently consider by Sandbakk *et al.* [171] in the context of coupled ion and volume transport in ion-membrane thermoelectrics.

In the case of $\nabla h = 0$, the Seebeck expressed in terms of Equation 8.5 is:

$$\alpha = \frac{\nabla V}{\nabla T}_{J_e=0,\,\nabla h=0} = \frac{-1}{q}\frac{{}^3L_{se}}{{}^3L_{ee}} \tag{8.7}$$

This gives the same form as that of Equation 8.6, except that there may be some external dissipation due to $J_m \neq 0$ that limits the heat to electron conversion efficiency possible. The conditions of a normal thermoelectric may be thought of as having $L_{mm} = 0$, so that $J_m = 0$ implies $\nabla h = 0$ — and there is therefore neither co-transport or dissipation. The other transport coefficients (σ, κ) will behave similarly [171].

In the case of $J_m = 0$, the Seebeck expressed in terms of Equation 8.5 is:

$$\alpha = \frac{\nabla V}{\nabla T}_{J_e=0,\, J_m=0} = \frac{-1}{q}\frac{{}^3L_{se}}{{}^3L_{ee}}\left(\frac{1 - \frac{{}^3L_{ms}}{{}^3L_{mm}}\frac{{}^3L_{me}}{{}^3L_{es}}}{1 - \frac{{}^3L_{me}}{{}^3L_{mm}}\frac{{}^3L_{me}}{{}^3L_{ee}}}\right) \tag{8.8}$$

The expression $\frac{{}^3L_{ms}}{{}^3L_{mm}}$ is the equivalent to the Seebeck coefficient but associated with transport of m instead of electron transport. That is:

$$\alpha_m \equiv \left(\frac{\nabla h}{\nabla T}\right)_{\nabla\tilde{\mu}_e,\, J_m=0} = \frac{{}^3L_{ms}}{{}^3L_{mm}} \tag{8.9}$$

Like α, α_m has its own presence contribution and that may be defined as:

$$\alpha_{m,\,presence} = -\left(\frac{\partial s}{\partial m}\right)_{u,n} \tag{8.10}$$

The expression $\frac{{}^3L_{em}}{{}^3L_{ee}}$ is the co-transport of J_m with J_e when there is no driving force for direct transport of m. It will have its own presence contribution:

$$\left(\frac{J_m}{J_e}\right)_{\nabla T=0,\, \nabla h=0} \approx \left(\frac{\partial m}{\partial n}\right)_{u,s} \tag{8.11}$$

This expression will be most accurate if all transport of m is mediated by transport of the electrons. This is certainly the case in the spin-state enhancement of Seebeck observed in oxide thermoelectrics [109, 196]. Due to the independent mobility of ions in Ag_2Se and Cu_2Se, Equation 8.11 is here only an approximation.

By combining Equation 8.10 and Equation 8.11 into a single expression, a quasi-thermodynamics expression for the entropy co-transport Seebeck may be obtained. Lets call this term $\alpha_{order-entropy}$. It can be formulated in terms of the free energy density (f) and T as:

$$\alpha_{order-entropy} = \frac{-1}{q}\left(\frac{\partial f}{\partial m}\right)_{T,n}\left(\frac{\partial m}{\partial n}\right)_{T,s} \tag{8.12}$$

The behavior of the order-entropy contribution to Seebeck near the phase transition will depend on the behavior of the order parameter (m) near the phase transition. This is expressed as a polynomial expansion in m with phenomenological thermodynamic coefficients. For a first order transition the form is [32]:

$$f_{1st} = am^2 + cm^3 + bm^4 + hm \tag{8.13}$$

With a, b, and c thermodynamic coefficients The cubic term causes the first order transition. Equation 8.13 can be solved for m such that $f_{1st}(m, h = 0) = 0$. For example, under the condition $c \gg b$, a:

$$m = \begin{cases} \frac{-c}{b} & T < T_c \\ 0 & T > T_c \end{cases} \tag{8.14}$$

From Equation8.14 $\frac{\partial m}{\partial n}$ will be a value that is dependent on the systems microscopics below T_c as expressed in the quantities b and c. Above the phase transition $\frac{\partial m}{\partial n}$ must be zero, because m is zero. By substituting Equation 8.14 in Equation 8.13 the relation $\left(\frac{\partial f}{\partial m}\right)_{T,n} = h$ is determined. Though there is no externally applied h, there is an internally induced h. The temperature gradient will induce a gradient in the order parameter. That order parameter gradient must induce a restoring force through a non-zero h. Using the functional forms of $\frac{\partial m}{\partial n}$ and $\frac{\partial f}{\partial m}$ described above, Equation 8.12 indicates that a first order transition may have a step change in $\alpha_{order-entropy}$ at T_c. An order entropy induced step change in Seebeck would explain the increase in the Seebeck and zT of Ag_2Se in its ordered phase.

Below a second order transition, the order parameter follows a critical power law. As dicussed in Chapter 5 it is characterized by a critical exponent, $m = m_0\tau_r^\beta$, with reduced temperature $\tau_r \equiv (T_cT)/T_c$ and $\beta > 0$. The Seebeck coefficient should also include a critical exponent contribution and be of form:

$$\alpha = \alpha_0 + \alpha_1 \tau_r^r, \tag{8.15}$$

in which α_0 and α_1 may have a separate temperature dependence.

Laguesse et al [115] suggested that Seebeck should have a critical exponent of $r = 1 - \lambda$, where λ is the critical exponent for heat capacity. As λ is less than unity, Laguesse et al. predicted r to be greater than 0. This would imply no Seebeck peak and thereby contradict both our observations in Cu_2Se [23] and also the critical exponent of $r = -1$ that Laguesse et al. measured in $YBa_2Ca_3O_{7-y}$ [115]. If h is large (relative to τ_r^{Δ}, where Δ is the gap exponent) [95], then the critical exponent for Seebeck will be larger than $1 - \lambda$. The free energy can be expressed as [95]:

$$f_{2nd} = \begin{cases} f_0 \tau_r^{2-\lambda} & \text{h small} \\ f_1 \tau_r^{\beta} & \text{h large} \end{cases} \tag{8.16}$$

A form for $\frac{\partial f}{\partial n}$ can be obtained from Equation 8.16:

$$\alpha_{order-entropy} = -\frac{\partial f_{2nd}}{q \partial n} = \begin{cases} \alpha_1 \tau_r^{1-\lambda} \frac{\partial T_c}{\partial n} & \text{h small} \\ \alpha_2 \tau_r^{\beta-1} \frac{\partial T_c}{\partial n} & \text{h large} \end{cases} \tag{8.17}$$

From Equation 8.17b if h is large enough, the critical exponent for Seebeck is $r = \beta - 1$. As β is typically a small fraction of unity, r should be slightly more than -1. That critical exponent is consistent with that measured in both our work on Cu_2Se and the work by Laguesse et al. on $YBa_2Ca_3O_{7-y}$ [115]. The form in of Equation 8.17b can also be determined from our Equation 8.13 and the definition of $m(T)$:

$$\frac{\partial m}{\partial n} = m_0 \tau_r^{\beta-1} \frac{T}{T_c^2} \frac{\partial T_c}{\partial n} \tag{8.18}$$

As per our discussion of the first order transition, the temperature gradient will induce $h \neq 0$. Therefore $\left(\frac{\partial f}{\partial m}\right)_{T,n} = h$ is non-zero. If this is applied with Equation 8.18 to

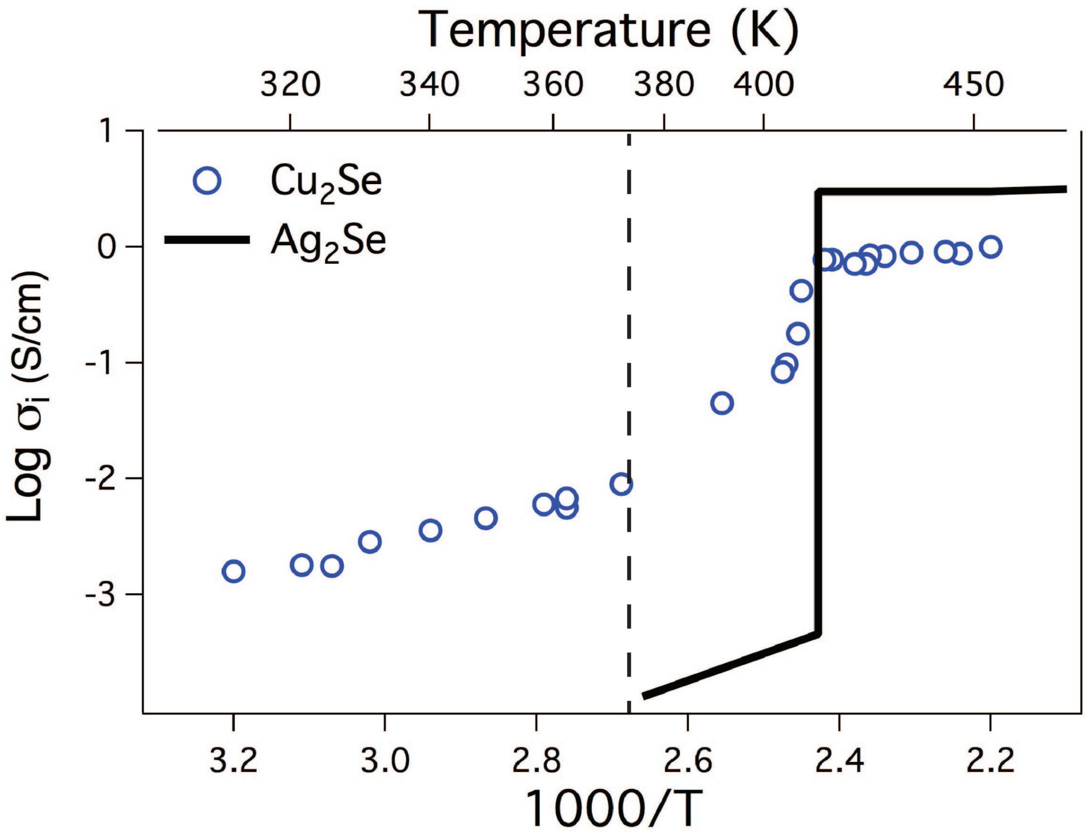

Figure 8.2: Ion conductivity of Cu_2Se [84] and Ag_2Se [136] through their phase transitions. Ag_2Se shows a step increase in ion conductivity at its phase transition, while Cu_2Se shows a super-exponential increase in ion conductivity to the phase transition temperature. The dotted line corresponds to 374 K, at which temperature the super-exponential increase begins.

Equation 8.12, the form and critical exponent of Equation 8.17b are obtained.

8.2 Ion-mediated Enhancement

When considering the specific case of super-ionic transitions, ionic transport properties may function as a convenient and metrologically tractable proxy for measurements of the order parameter. A super-ionic transition is a disordering of mobile ions that results in a substantial change in ionic transport properties. The enhancements in ionic transport may be much more significant than those of electronic transport, and the phase transition may act on the electrons indirectly through the ions. In this case we have:

$$\frac{\partial T_c}{\partial n} = \frac{\partial T_c}{\partial n_i}\frac{\partial n_i}{\partial n} \tag{8.19}$$

Where n_i is the concentration of mobile ions. If ionic transport is directly enhanced by the phase transition, $\frac{\partial T_c}{\partial n_i}$ will be non-zero.. Such a variation has been observed in both Cu_2Se [194] and Ag_2Se [15] as well as other super-ionics [111, 114]. Electrons and ions may interact through both chemical and electrostatic processes; their co-transport interaction would indicate a significant value for $\frac{\partial n_i}{\partial n}$. Polarization measurements of some oxygen conductors have revealed such coupled transport [205, 119, 36], which has been explained as being due to a long range electrostatic interaction changing the effective charge of the transported ions [99]. As $\frac{\partial T_c}{\partial n}$ and $\frac{\partial \alpha}{\partial n}$ may be obtainable via gated transport measurements [172], future studies may be able to precisely test Equation 8.17b.

Super-ionic materials are defined phenomenologically as those with ion conductivity greater than 1 S/cm at elevated temperatures [21, 87, 163]. They are divided into three classes by the manner in which they achieve high ion conductivity. Type III super-ionics are those without a phase transition (*e.g.* β-Alumina) [21] and therefore are not of interest here. This study is of the ordered or non-superionic phase of both Ag_2Se and Cu_2Se and therefore their classification within the broader contexts will be helpful in finding similar materials.

Type I and type II super-ionic conductors are characterized by a structural phase transition with an entropy change close to that of melting (i.e. order $10\,\mathrm{JK^{-1}mol^{-1}}$ and a concurrent increase in ion conductivity [151]. For type I super-ionic conductors there is a sudden enthalpy release at the phase transition temperature (i.e. a first order phase transition) and a concurrent discontinuous increase in ionic conductivity [21]. For type II super-ionic conductors the ionic conductivity increases super-exponentially up to the phase transition temperature, the structure changes continuously, and there is a lambda-shaped peak in heat capacity like that characteristic of a second order phase transitions [87].

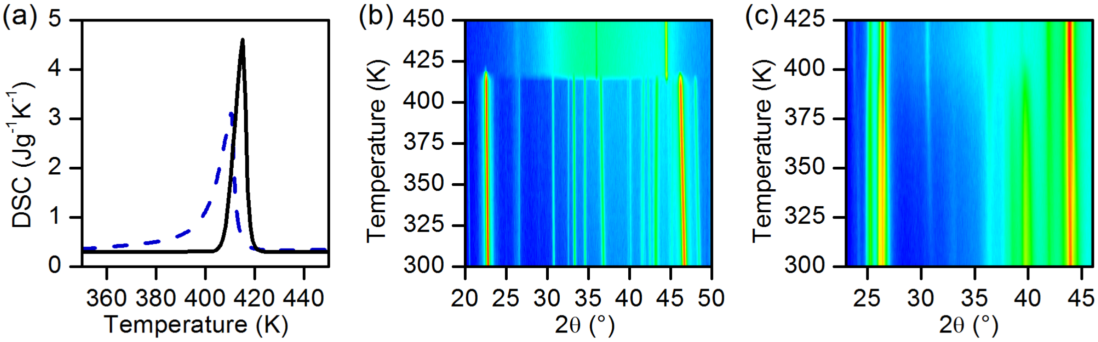

Figure 8.3: Calorimetry data (a) for Ag_2Se (solid line) and Cu_2Se (dotted line) on heating. Ag_2Se shows a characteristic symmetric peak in its DSC curve due to the enthalpy release of its first order phase transition. Cu_2Se shows an extended asymmetric elevation in its heat capacity due to its second order phase transition. Temperature resolved powder X-ray diffractograms of Ag_2Se (b) and Cu_2Se (c). The structural transformation of Ag_2Se is first order, while that of Cu_2Se is second order.

To determine whether a material in this study has a type I or type II super-ionic phase transition, three physical properties are examined through the phase transition: ionic conductivity, calorimetry, and crystallographic structure. A type I super-ionic transition (typically first order) is characterized by a sudden disordering of the ions [21, 87, 151]. As the number of mobile ions and their diffusivity increase suddenly, they show a concurrent step increase in ion conductivity. Literature results show that Ag_2Se ion conductivity increases by four orders of magnitude at 412 K, see Figure 8.2 [136] The disordering of the ions requires the absorption of enthalpy. DSC data for Ag_2Se shows a sharp symmetric peak centered at 414 K, see Figure 8.3(b). As the ordering of the ions is lost suddenly, there should be a corresponding change in the crystal symmetries represented by disappearance of peaks in the diffractogram. Temperature resolved PXRD shows numerous strong crystallographic peaks disappearing at the phase transition temperature, see Figure 8.3(b), indicative of a sudden disordering of the Ag ions.

In a type II super-ionic phase transition the ions disorder continuously (as in a second order transition) until the phase transition temperature is reached. The ionic conductivity increases super-exponentially below the phase transition temperature [21, 87, 151]. Horvatic et al. measured such a super-exponential increase in the ionic conductivity of Cu_2Se, see Figure 8.2 [84] As the ionic disordering occurs continuously over a significant temperature range, the heat capacity is elevated over that range [151]. The DSC data for Cu_Se shows a broad asymmetric lambda peak, see Figure 8.3(a). Its crystal structure indicates gradual disordering and a second order phase transition, see Figure 8.3(c). From the behavior of its ionic conductivity, heat capacity and crystallography through its phase transition temperature, we conclude that Cu_2Se has a type II super-ionic phase transition.

Experimentally, we have seen an example of the contrast between a type II and type I super-ionic thermoelectric material in Ag_2Se and Cu_2Se. Consider transport of heat, ions, and electrons:

$$du = Tds - \tilde{\mu}_e dn_e - \tilde{\mu}_i dn_i \tag{8.20}$$

The corresponding entropy production is:

$$T\dot{S} = -J_s \cdot \nabla T J_e \cdot \nabla \tilde{\mu}_e J_i \cdot \nabla \tilde{\mu}_i \tag{8.21}$$

The corresponding Onsager relationships are [132]:

$$\begin{bmatrix} J_e \\ J_i \\ J_s \end{bmatrix} = - \begin{bmatrix} {}^3L_{ee} & {}^3L_{is} & {}^3L_{es} \\ {}^3L_{ie} & {}^3L_{ii} & {}^3L_{is} \\ {}^3L_{se} & {}^3L_{si} & {}^3L_{ss} \end{bmatrix} \begin{bmatrix} \nabla \tilde{\mu}_e \\ \nabla \tilde{\mu}_e \\ \nabla T \end{bmatrix} \tag{8.22}$$

If the Seebeck coefficient is measured in an open circuit system with ion blocking electrodes (*i.e.* $J_i = 0,\ J_e = 0$):

$$\alpha = \frac{\nabla V}{\nabla T}_{J_e=0,\, J_i=0} = \frac{-1}{q} \frac{{}^3L_{se}}{{}^3L_{ee}} \left(\frac{1 - \frac{{}^3L_{iq}}{{}^3L_{ii}} \frac{{}^3L_{ie}}{{}^3L_{eq}}}{1 - \frac{{}^3L_{ie}}{{}^3L_{ii}} \frac{{}^3L_{ie}}{{}^3L_{ee}}} \right) \tag{8.23}$$

The first term in the numerator is the band structure electronic Seebeck. The second term in the numerator is the Seebeck enhancement due to the ions. The term in the denominator is an ionic drag term. The ionic drag term will be small because

$L_{ii} \ll L_{ee}$ and L_{ie} is even in the largest measured case only on the order of L_{ii}. If L_{is} and L_{ie} are significant compared to L_{es} and L_{ee}, analysis of only electronic properties will lead to an incomplete description of the thermoelectric properties.

The first condition for the ion transport enhancing Seebeck is that $\frac{L_{ie}}{L_{ee}} = \frac{\sigma_{ie}}{\sigma_{ee}}$ be large. $\frac{L_{ie}}{L_{ee}} = \frac{\sigma_{ie}}{\sigma_{ee}}$ is the ratio between ions transported and electrons transported under a gradient in $\tilde{\mu_e}$ but no gradient in $\tilde{\mu_i}$. Mixed ion-electron conductors can show electron-ion transport coupling. Electrons and ions may interact through both chemical and electrostatic processes. Polarization measurements of some oxygen conductors have revealed such a coupling [205, 119], which has been explained as due to a long range electrostatic interaction changing the effective charge of the transported ions [99]. Thus in both low temperature type I Ag_2Se and type II Cu_2Se $\frac{L_{ie}}{L_{ee}}$ may be significant. In the high temperature phase of Ag_2Se $\frac{L_{ie}}{L_{ee}}$ has been measured to be less than 10^{-2} [137]. This has been explained by Ogawa and Kobayashi [141, 142] to be due to the high concentration of ionic carriers. In the super-ionic limit they found that $\frac{L_{ie}}{L_{ii}} < \frac{n_e}{n_i}$. n_i is much larger in the superionic phase than the ordered phase [142].

The second condition is that ionic Seebeck, $\alpha_i = -\frac{L_is}{L_ii}$ be significant. The coupling of concentration of Ag and Cu to the thermodynamics of disordering has been observed via the dependence of T_c on composition in Cu_2Se [194] and Ag_2Se [15]. Mechanistically this may function through a dependence of occupation of soft modes (*e.g.* the Zn_4Sb_3 rattler) [173] on the concentration of Ag^+ and Cu^+. An observation of not only structural entropy change at the phase transition but also of structural entropy transport is given by Korzhuev and Laptev [107]; they measured a sharp peak in the thermodiffusion of Cu^0 in Cu_2Se at the 410 K phase transition. From this they calculated a heat of transport of $Q^*_{Cu^0}$ of Cu atoms of 1 eV. Conservation of particles and charge requires that:

$$Q^*_{Cu^0} = Q^*_{Cu^+} Q^*_p = qT(\alpha_{Cu^+} - \alpha) \tag{8.24}$$

Therefore $Q^*_{Cu^0} = 1\,eV$corresponds to $\alpha_{Cu^+} \approx 2500\,\mu V/K$ at the phase transition. If even 2% small fraction of this copper entropy were co-transported with Cu_2Se, than the Seebeck and zT enhancement observed would be completely explained.

8.3 Future work

Other super-ionic materials should be evaluated for their phase transition thermoelectric properties. The thermoelectric materials Ag_2S, Ag_2Te, Cu_2S, and Cu_2Te are all type I super-ionics [87]; like Ag2Se, they are not expected to show phase transition enhanced Seebeck. There are many other known type II super-ionic conductors [21] such as PbF_2 [9, 34] and K_2S [51]. Like Cu_2Se they have a modified fluorite (or anti-fluorite) structure. Because of their large band gaps, their thermoelectrics properties are unexamined. It may be possible to change Ag_2Se from a type I to a type II superionic material. The order of the phase transition has been changed in certain super-ionic materials by alloying. PbF_2 is type II super-ionic. Alloying it with KF changes the temperature dependence of its ionic conductivity. At 10% KF and above it becomes a type I super-ionic [86]. Though AgI is type I, $RbAg_4I_5$ has both a type I and type II super-ionic transition [93]. Additionally, when a pressure of 2.6 GPa is applied to AgI, it becomes a type II super-ionic conductor [97].

Critically increased entropy may be present in other materials systems. $AgCrSe_2$ [66] which is also an ion transporting materials shows a small Seebeck enhancement near a phase transition, though there is no evidence that this is associated with critical phenomena. The temperature of the continuous transition in the CuI-AgI system shows a composition dependence [114]. The effect on Seebeck from order entropy is likely not limited to mixed ion-electron conductors. Any material in which the entropy associated with a phase transition might be coupled to transport is a candidate. For example, the magnetic ordering phase transition associated with giant magnetoresistance is often accompanied by a corresponding significant Seebeck change [91, 120]. Applying a magnetic field to these materials induces ordering and results in a corresponding reduction in Seebeck.

In order to understand and engineer this phenomenon, substantial future work needs to be done. The ionic properties, both the conductivity [107] and the Seebeck, [12] may need to be measured and considered when engineering these materials. Further synchotron and neutron crystallographic work may be able to uncover the structure and order parameter. The Onsager coefficient analysis above may be used to relate separate measurements of ion and electronic properties, in order to directly test the hypothesis of ion-mediated or perhaps even order-mediated Seebeck enhancment.

The best thermoelectric performing materials in this class of compound are yet to be synthesized. Through such future work a greater understanding of the excellent thermoelectric properties of the ordered phases of super-ionic materials may be understood and engineered.