

A Phenomenological Model of Unconventional Heat Transport Induced by Phase Transition in Cu_{2-x}Se

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Research in copper selenide thermoelectric (TE) alloys has raised the possibility of a significant enhancement of the TE figure-of-merit ZT when the Seebeck coefficient is affected by a concurrent phase transformation. This ZT increase has also been related to a radical reduction of the thermal conductivity evaluated by transient laser flash thermal diffusivity measurements. In contrast, steady-state Harman-based measurements do not support a significant ZT increase only a modest one, because the thermal conductivity instead of decreasing goes through a sharp maximum as it approaches the critical phase transformation temperature of 407 K. The nature of this sharp increase of heat transfer has not been related to the well-known electronic or phononic contributions. Below the critical temperature, when the alloy is exposed to a steady-state temperature gradient, an additional heat transfer phenomenon takes place, induced by the ongoing gradual phase transition. We show that the enthalpy associated to the α to β and β to α phase transformations can lead to heat flow in the direction of the temperature gradient above and beyond conventional heat conduction. This unconventional heat transfer mechanism disappears when the temperature rises above the critical temperature where only a stable β phase remains. We propose a model of such a heat transport which leads to the sharp maximum of the related thermal conductivity. Numerical results obtained from the model compare favorably to the experimentally measured thermal conductivity.

Key words: Figure-of-merit, thermal conductivity, phase transition, thermoelectric measurements, ZT -Scanner, Harman method, Cu_2Se

INTRODUCTION

Copper selenide and materials closely related to this composition^{1–8} have attracted attention mainly due to two reasons. At first, these materials demonstrated decent thermoelectric performance in the 700–800 K temperature range.^{1,2} In addition, several publications have described an extremely high figure-of-merit around 410 K. Values of the dimensionless figure-of-merit ZT up to 2.4 have been reported¹ for Cu_2Se in the narrow temperature

interval where a structural phase transition occurs. This high performance was related to the drastic decrease of the thermal conductivity as evaluated by transient laser flash thermal diffusivity measurements.^{1–8} In contrast, more recent⁹ steady-state Harman-based measurements of Cu_{2-x}Se do not support a significant increase of ZT only a modest one, because the thermal conductivity instead of decreasing goes through a sharp maximum as it approaches the critical temperature of 407 K. We will discuss here the heat transfer phenomena in the temperature range limited by this phase transition regardless of the high-temperature TE properties of copper selenide and related compounds. The importance of the observed sharp maximum is

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not limited to the conclusion that the reported ultra-high TE performance of Cu_2Se is an artifact due to the wrong choice of measurement technique. It is rather the puzzling nature of the maximum of the thermal conductivity which signals a novel mechanism of thermal conduction. Our objective is to present a phenomenological model for this unconventional heat transfer mechanism made possible by the phase transition in Cu_{2-x}Se . Besides developing the ingredients of a model based on directional transport of the enthalpy changes associated with the phase transition, we use the data obtained from our measurements of the thermoelectric and thermal properties to obtain approximate quantitative expressions for the physical quantities involved. The numerical results obtained from the model can be compared favorably with the experimental data on the thermal conductivity.

EXPERIMENTAL DETAILS AND BASIC RESULTS

We studied a polycrystalline copper selenide $4.10 \text{ mm} \times 5.48 \text{ mm} \times 5.59 \text{ mm}$ sample with the nominal composition of $\text{Cu}_{1.985}\text{Se}$ provided by Northwestern University, and produced as described in Ref. 4. Two opposite sides of the sample were Ni electroplated and brazed with SnPb soldering alloy prior to mounting on a ZT-Scanner instrument.^{10–12} This sample has experienced several heating/cooling cycles over the temperature range covering the phase transition; however, we do not expect any significant changes of its composition. Nonetheless, we cannot guarantee that the stoichiometry of the sample has remained the same so we will describe it by the more general formula Cu_{2-x}Se . The ZT-Scanner¹⁰ employs a transient bipolar Harman procedure in which the sample is exposed to a sequence of two symmetrical pulses of direct current (100 mA; 5 min) of opposite polarities. These pulses follow one another after a period equivalent to the length of the pulse. This avoids introducing any possible preferential accumulation of Cu ions on either one of the sample extremities in these ionic conductors.

A detailed description of TE measurements with a ZT-Scanner and a differential scanning calorimetry (DSC) with a Setaram DSC-131 is provided in Ref. 9.

Harman-based measurements ensure a direct determination of the ZT and the electrical conductivity (σ) of the sample. Variation of ZT with temperature is shown in Fig. 1 (blue diamonds, scale on the left) which clearly demonstrates the impact of a phase transition around 400 K, similarly to the data published in Refs. 3–8.

The ZT-Scanner setup¹⁰ provides two thermocouples which deliver the temperature difference on the opposite sides of the sample, additionally allowing the direct evaluation of the Seebeck coefficient, α . The power factor¹³ (PF) defined as the product $\alpha^2\sigma$ is also shown as a function of temperature in Fig. 1

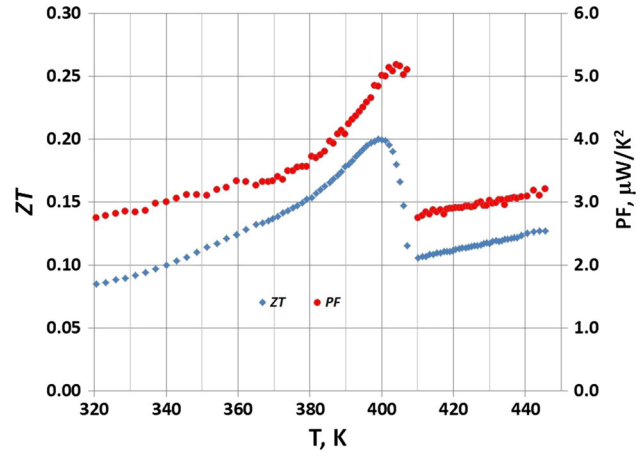


Fig. 1. Variation of ZT (blue diamonds, scale on the left) and PF (red circles, scale on the right) as the functions of temperature measured simultaneously by Harman setup on a Cu_{2-x}Se sample (Color figure online).

(solid red circles, scale on the right). It shows specific variation around the temperature of the phase transition similar to ZT . It is important to note that there is a shift between the temperatures of the peak positions of ZT and PF. This shift cannot be attributed to the insufficient precision of the temperature determination because α and σ were measured simultaneously with the ZT on the same temperature run.

This shift is a sign of sharp changes of the thermal conductivity, κ , because it is the only parameter left besides the PF in the expression for the ZT . Indeed, the blue diamonds in Fig. 2 show the variation of the thermal conductivity as a function of temperature with a sharp maximum at 407 K. The slight gradual decrease of κ on the low-temperature side of the peak is linked to the decrease of the electronic contribution, κ_e , to the total thermal conductivity. The electronic contribution, κ_e (solid red squares in Fig. 2), can be roughly calculated from the electrical conductivity data (inset in Fig. 2) using the value of Lorenz number of $2.44 \times 10^{-8} \text{ W}\Omega/\text{K}^2$ typical for degenerated semiconductors.¹⁴ Subtraction of the κ_e from the total conductivity, κ , usually gives the “lattice” contribution, κ_l , shown by the green triangles in Fig. 2. The significant sharp increase of the thermal conductivity near the critical point which appears in the lattice contribution, κ_l , is unlikely to be due to an increase in phonon heat transport because, in this temperature range, the material is less ordered, which would lead to additional phonon scattering and therefore a reduction of the phonon mean free path and phonon thermal conductivity. We interpret the experimental data as the observation of some additional heat transport which takes place only in the temperature range where there is an ongoing (gradual) phase transition. A similar peak related to a phase transition was observed¹⁵ in shape memory alloys, $\text{Ni}_{50}\text{Ti}_{50}$, but to the best of our

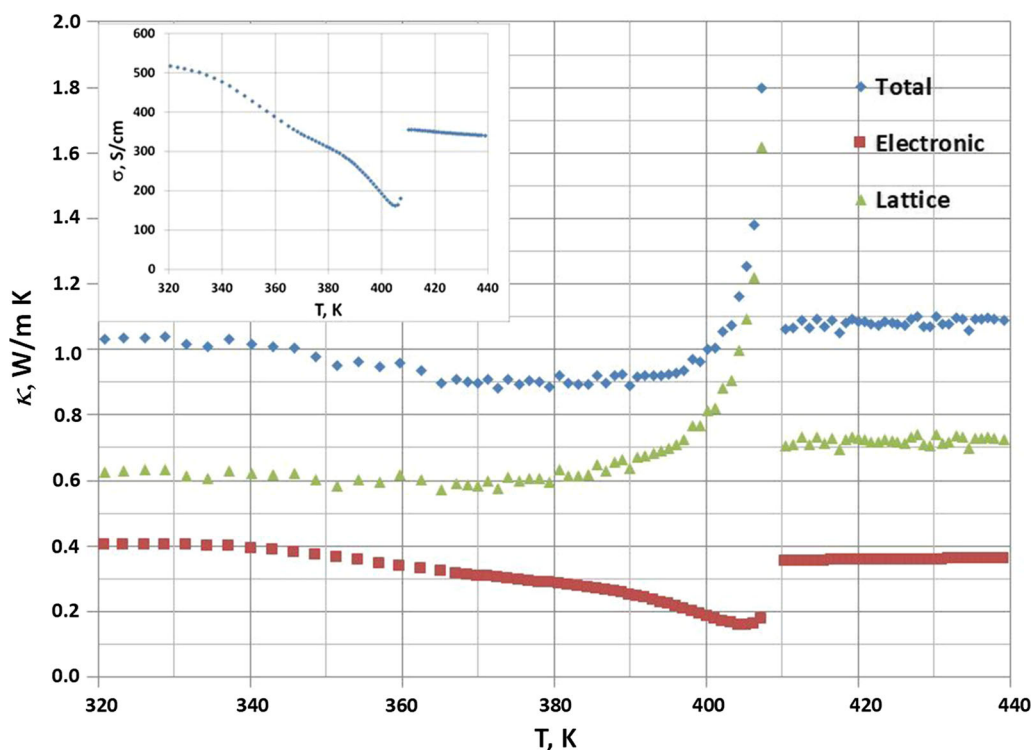


Fig. 2. Variation with temperature of the total thermal conductivity κ (blue diamonds, experimental data), electronic contribution κ_e (red squares, calculated using Lorentz number $L = 2.44 \times 10^{-8} \text{ W}\Omega/\text{K}^2$ and experimental data for σ shown in inset of this figure) and lattice thermal conductivity κ_l (green triangles, calculated by subtraction of κ_e from κ) (Color figure online).

knowledge there is no description of such mechanism in the literature. Therefore, in the following section, we will formulate a phenomenological model of this unconventional heat transfer mechanism induced by a gradual phase transition in the Cu_{2-x}Se sample.

PHENOMENOLOGICAL MODEL

The central idea of the proposed model is based on the observation that, during the first order phase transformations, occurring in both directions, there is a continuing local enthalpy absorption/release. When the sample under study is subjected to a temperature gradient during the measurement, this enthalpy transfer can be responsible for the additional heat transport along the sample.

The most comprehensive description of the phase transition phenomenon in copper selenide is presented in Ref. 4. For a given stoichiometric ratio, as the temperature increases both the α (low-temperature) and β (high-temperature) phases coexist in an extended temperature interval. The ratio of the relative concentrations, N_β/N_α , of these phases gradually increases with temperature from 0 to 1 until the transformation is completed at the critical point where the high-temperature phase, β , occupies 100% of the volume. As a consequence, when a temperature gradient is imposed on such samples, steady-state concentration gradients of both phases will be formed

in the material. The concentration N_β of the β phase will decrease in the direction of decreasing temperature while the α phase will show the inverse tendency. Obviously, N_α and N_β are interrelated by the simple equation $N_\alpha + N_\beta = 1$, and in what follows we will describe the heat transfer phenomenon only from the point of view of the β phase.

From general principles, we know that, if a gradient of some physical substance is present, then naturally occurring statistical processes will establish a diffusion flow of this substance in the direction opposing the gradient, with the tendency to homogenize in space the concentration of the given substance. If some external driving force maintains the gradient constant in time, then a steady diffusion flow is observed much like the diffusion current of electrons in a semiconductor with an imposed temperature gradient. In a case of a Harman-based measurement, a steady-state temperature gradient is imposed on the sample,^{16,17} and this gradient is at the origin of the gradient of the β phase concentration in the copper selenide sample.

Looking at the atomic scale to an arbitrary cross-section perpendicular to the heat and electrical current flow through the sample, we would observe that the unit cells with a β phase structure are more abundant on the high-temperature side than on the low-temperature side. This distribution will tend to propagate this crystal symmetry towards the cooler side. As this transfer occurs, the newly generated fraction of the β phase will become excessive

compared to the equilibrium for the lower local temperature value, leading to a spontaneous return to the low-temperature α phase with a concomitant release of heat equivalent to the enthalpy change of the phase transition. This process will happen at each cross-section from the sample extremity in contact with the high-temperature source (providing an additional amount of heat) down to the one in contact with the low-temperature sink (releasing that heat). Continuous statistical repetitions of these phase transformation events at each cross-section will result in an additional net steady heat flow through the sample with the direction opposite to the imposed temperature gradient. Note that this process will provide an additional steady-state pathway for heat transfer, which would be absent if the sample did not undergo a gradual phase transition, and in fact it disappears once the temperature exceeds the critical phase transformation temperature and the sample has been homogeneously transformed to the single β phase.

NUMERICAL SIMULATION AND DISCUSSION

For the numerical simulation of this heat transfer phenomenon induced by the phase transition, we can limit ourselves to a one-dimensional model of propagation along the sample length described by the coordinate x , and cross-sectional area A , and write the equations that follow.

Consider first the contribution κ_{pt} to the thermal conductivity of heat flux through a specimen of cross-section A at position x :

$$J_{\text{Q}} \left[\frac{\text{W}}{\text{m}^2} \right] = -\kappa_{\text{pt}} \frac{dT}{dx} \quad (1)$$

If κ_{pt} describes the thermal conductivity due to phase change enthalpy transfer, then the same flux can be expressed as a diffusive transport of the enthalpy change (per unit of mass) for the phase transformation in copper selenide (Δh_{CS}):

$$J_{\text{Q}} = \Delta h_{\text{CS}} \rho D(T) \left(-\frac{\partial N_{\beta}}{\partial x} \right) \quad (2)$$

where $\rho = 6.3 \times 10^6 \text{ g/m}^3$ is the mass density of copper selenide and $D(T)$ is a temperature-dependent diffusion coefficient (m^2/s) which represents the propagation of the β phase when there is a gradient of its relative concentration, N_{β} .

From Eqs. 1 and 2, we can express the thermal conductivity related to the contribution of the discussed unconventional heat transfer phenomenon:

$$\kappa_{\text{pt}} = \Delta h_{\text{CS}} \rho D(T) \frac{\partial N_{\beta}}{\partial T} \quad (3)$$

As it can be seen from Eq. 3, the temperature dependence of $\kappa_{\text{pt}}(T)$ is defined by $D(T)$ and by

$N_{\beta}(T)$. The temperature dependence of the relative concentration of the β phase can in principle be estimated from the phase diagram⁴; however, this approach lacks sufficient precision for our numerical simulation purpose. Therefore, we have opted for an approach based on experimental data obtained for our sample by differential scanning calorimetry (DSC). In Ref. 9, we have shown that the maximum peak of the specific heat as a function of increasing temperature is a result of the continuous reduction of the material fraction of the low-temperature α phase transforming to the β phase. Assuming this, the mass fraction of β phase can be expressed as

$$N_{\beta} = \Delta c_{\text{p}}(T) / \Delta c_{\text{max}} \quad (4)$$

where $\Delta c_{\text{p}}(T)$ is the measured value of the apparent heat capacity for a given temperature after subtraction of the Dulong–Petit baseline and $\Delta c_{\text{max}} = 2.617 \text{ J/gK}$ is its maximum value at the critical temperature. The integral over T of $\Delta c_{\text{p}}(T)$, or equivalently the area under the curve on the DSC curve, is equal to the enthalpy per unit of mass of the phase transition (Δh_{CS}) in copper selenide.

Combining Eqs. 3 and 4 and assuming the usual activated expression for the diffusion coefficient $D(T) = D_0 \exp(-\Delta E/kT)$, where D_0 is assumed to be temperature independent, we obtain:

$$\kappa_{\text{pt}} = (\Delta h_{\text{CS}} / \Delta c_{\text{max}}) \rho D_0 \exp(-\Delta E/kT) \frac{\partial \Delta c_{\text{p}}}{\partial T} \quad (5)$$

Figure 3 shows the DSC specific heat measurements performed on our sample with the heating rates (V_{h}) of 3 K/min and 6 K/min. Numerical integrations of the data from Fig. 3 result in close values (31.1 J/g and 30.5 J/g, respectively) for Δh_{CS} which is close to the reported value in Ref. 4. We will use the average value of 30.8 J/g for Δh_{CS} in the numerical simulation.

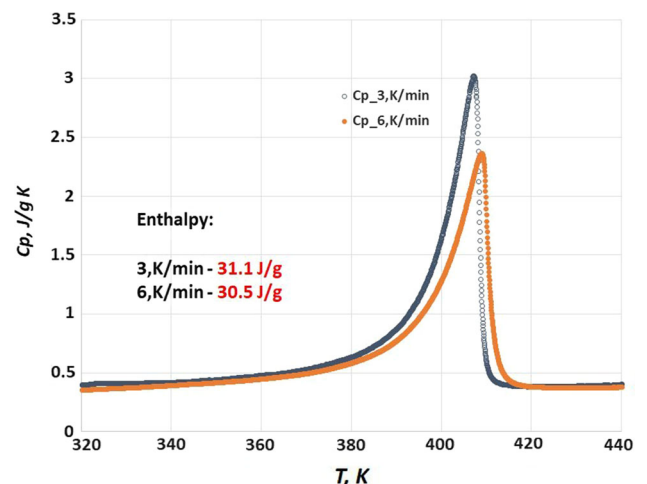


Fig. 3. DSC specific heat measurements on Cu_{2-x}Se sample with the heating rates (V_{h}) of 3 K/min and 6 K/min (Color figure online).

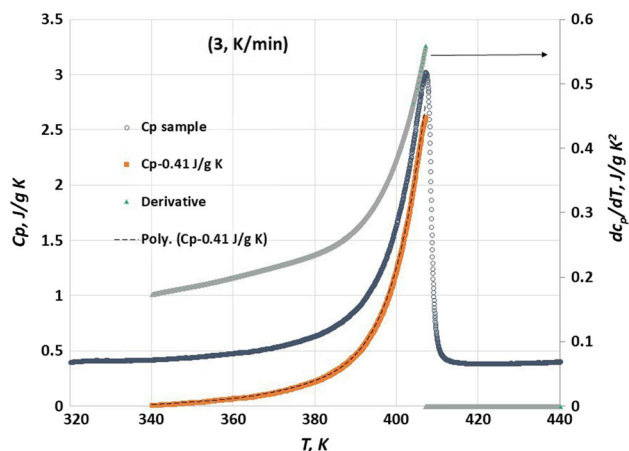


Fig. 4. Experimental DSC specific heat curve (blue open circles) measured on Cu_{2-x}Se sample at heating rate 3, K/min, $\Delta c_p(T)$ (orange line), obtained by subtraction of the Dulong-Petit baseline value (0.41 J/g K in our case) from the experimental DSC curve, 6th order polynomial trend line for $\Delta c_p(T)$ data (black dashed line) and derivative $\frac{\partial \Delta c_p}{\partial T}$ (gray line, scale on the right) (Color figure online).

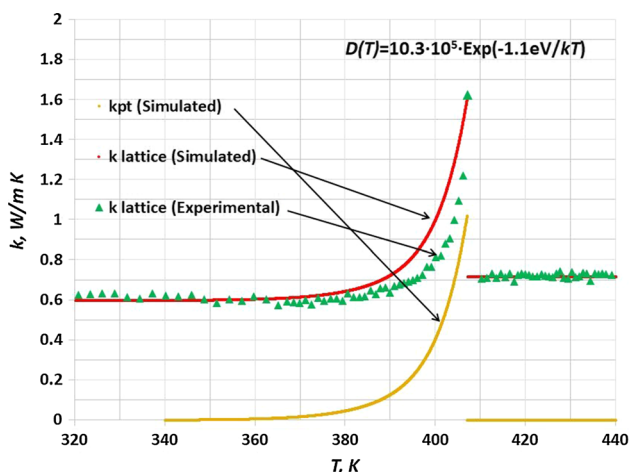


Fig. 5. Simulated variation of κ_{pt} in the Cu_{2-x}Se sample using $D_0 = 10.3 \times 10^5 \text{ m}^2/\text{s}$ (yellow line), simulated lattice contribution κ_l (red line, obtained by addition of two constant values to the above numerically simulated κ_{pt} : 0.6 W/m·K below and 0.72 W/m K above the critical temperature) and experimental data for κ_l from Fig. 2 (green triangles). Note that what is called the lattice contribution also contains the contribution from κ_{pt} (Color figure online).

The shift to a higher temperature of the peak of the DSC curve measured at a higher heating rate V_h is due to the thermally activated nature of the phase transition.¹⁸ An Arrhenius plot of V_h/T_{max}^2 versus temperature, obtained from our Fig. 3, gives the value 1.1 eV for the energy of activation ΔE of the phase transition reaction as it follows from Kissinger's description of reaction kinetics in differential thermal analysis.¹⁹ It is logical to use this value in Eq. 5 for ΔE as the parameter controlling the diffusive-like propagation of the β phase.

There is another quantity $\frac{\partial \Delta c_p}{\partial T}$ which is needed in Eq. 5 in order to numerically simulate the temperature dependence of κ_{pt} . Ideally, infinitely slow

measurements should be used to evaluate $\Delta c_p(T)$ so for the numerical simulation, we used the experimental data obtained for the lower heating rate. The orange square points on Fig. 4 show $\Delta c_p(T)$ which is obtained by subtraction of the Dulong-Petit baseline value (0.41 J/g K in our case) from the experimental DSC curve measured with the 3 K/min heating rate. The temperature interval of interest extends up to 407 K where the curve reaches the maximum. By establishing this upper limit, it was possible to obtain a high precision polynomial tendency line valid up to this point. A corresponding polynomial of degree 6 was obtained with the coefficients defined up to the 6th digit after the decimal point (see the discontinuous dark tendency line with $R^2 = 9.998$ in Fig. 4). The derivative with respect to temperature of this polynomial is also presented (right scale) in Fig. 5 by the gray line where we have imposed the zero value for the derivative for temperatures above the maximum of DSC curve.

Now all the parameters and functions of Eq. 5 have been defined, except for the pre-exponential phenomenological coefficient D_0 . By varying this parameter, we obtain the best fit with the value $D_0 = 10.3 \times 10^5 \text{ m}^2/\text{s}$. The orange curve in Fig. 5 shows the simulated variation of κ_{pt} in the Cu_{2-x}Se sample.

The simulated lattice contribution κ_l presented by the continuous red line on Fig. 5 is obtained by the addition of two constant values to the above numerically simulated κ_{pt} : 0.6 W/m K below and 0.72 W/m K above the critical temperature. We used here two values instead of one because the experimental observation of the true lattice contribution leads to slightly different lattice thermal conductivity values for the α and β phases. Figure 5 favorably compares the simulated dependency from our model to the experimental variation of κ_l . Both curves demonstrate similar sharp peaks in the temperature interval of the phase transition. The slightly less pronounced sharpness of the simulated curve may be related to the use of the DSC results for finite heating rate instead of an infinitely low rate in an ideal case, applicable to a steady-state description.

We have formulated our phenomenological model of heat conduction without speculating on the kind of atomic displacements which could lead to a diffusive-like propagation of the β phase towards lower temperatures, and we have obtained the diffusion coefficient for this process $D(T) = 1.03 \times 10^6 \text{ m}^2 \text{ s}^{-1} \exp(-1.1 \text{ eV}/kT)$. We know that Cu ions are highly mobile in this high-temperature phase of copper selenide, and it is tempting to suggest that movement of these ions may be involved. To this end, we have used the temperature dependence of the diffusion coefficient $D_{\text{Cu}}(T) = 8.5 \times 10^{-8} \exp(-3960 \pm 600 \text{ J/mol}/RT) \text{ m}^2 \text{ s}^{-1}$ of Cu in $\text{Cu}_{1.8}\text{Se}$ from reference Ref. 20, and calculated the value $2.64 \times 10^{-8} \text{ m}^2/\text{s}$ at 407 K, which is close to

$D(T = 407 \text{ K}) = 2.46 \times 10^{-8} \text{ m}^2/\text{s}$. The similarity between the two coefficients at the critical temperature should not be considered as a proof of the validity of our model, but it does show that the value of the pre-exponential factor, D_0 , is reasonable when combined with the experimentally defined activation energy of 1.1 eV. Note, however, that the unconventional heat transfer we have described in the proposed model is not to be associated to the continuous diffusion of Cu ions, or other elements, from one end of the sample to the other, as this transfer of atoms does not occur. Instead, the migration of interfaces between the α and β phases is associated with very slight displacement of the atoms, on a distance typically shorter than the interatomic distance, and the effective mobility is of the same order of magnitude as the one for atomic diffusion of Cu.

CONCLUSIONS

Steady-state Harman-based measurements and calculations of the thermal conductivity have shown a sharp increase of heat transfer near the critical point of a first-order (and gradual) phase transition which cannot be related either to the electronic or the phonon contributions. We have proposed a phenomenological model for this unconventional heat transfer mechanism induced by the phase transition in solid Cu_{2-x}Se in the temperature range where two phases coexist. We have argued that, when the material is subjected to a temperature gradient, this gradient maintains a concomitant gradient of both phases for temperatures in this range. Heat injection at the high-temperature contact to the sample flows through it by continuing local enthalpy absorption/release as the first-order phase transformations occur in both directions to maintain a stationary value of the α and β phase concentration corresponding to the temperature at each point in the sample. We have shown that maintaining the phase gradient can be responsible for the additional net heat transport in the direction of the temperature gradient and have provided an equation for κ_{pt} , the additional contribution to the thermal conductivity describing this process. A numerical simulation of the temperature behavior of κ_{pt} compares favorably with the experimental measurements. Our contribution shows that, besides the well-known heat transport mechanisms such as phonon propagation and free charge carrier transport including ambipolar diffusion, there is another heat transport mechanism which to the best of our knowledge has never been described. This unconventional heat transport takes place in solids undergoing a gradual structural phase

transition. In this sense, the importance of this result is not limited to a better understanding of the TE performance of the Cu_{2-x}Se compounds as it can be related to the fundamentals of solid-state science.

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