

# Supplementary Material

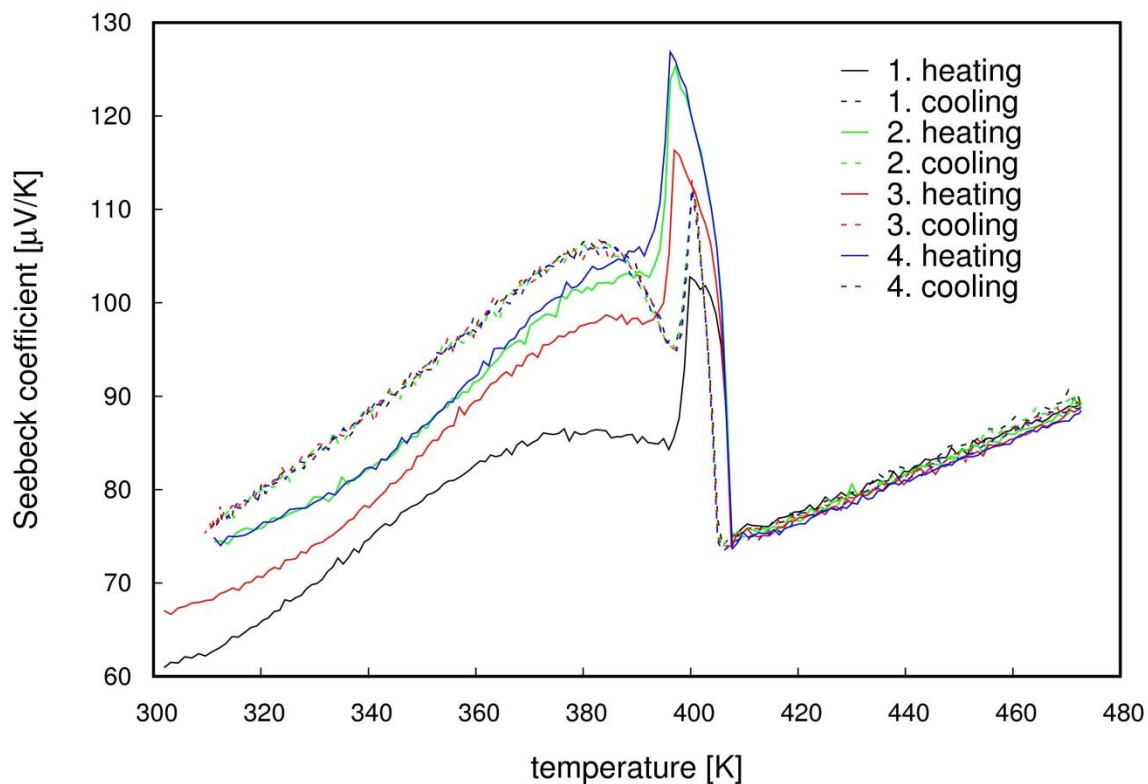
for

## The unstable thermoelectric effect in non-stoichiometric $\text{Cu}_2\text{Se}$ during the non-equilibrium phase transition

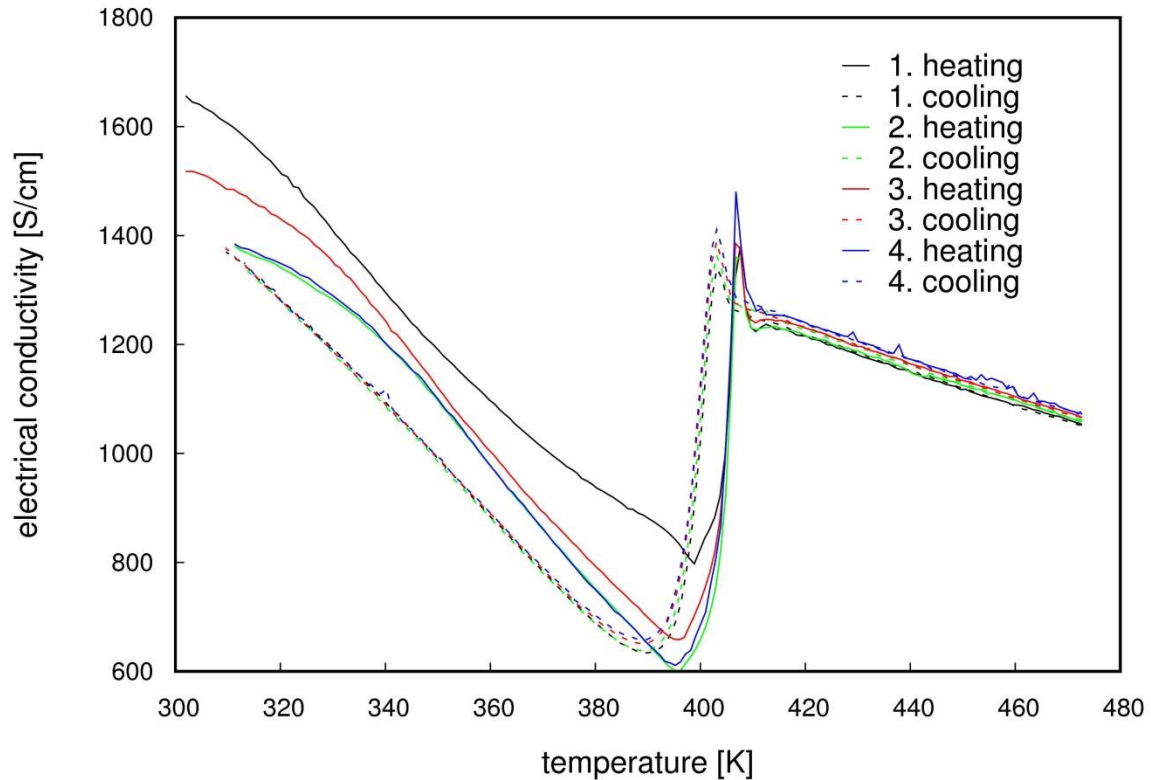
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### 1. Reproducibility of the phase transition

Two measurements of thermoelectric properties were performed with an effective heating/cooling rate equal to 1.2 K/min. The measurements consisted of two thermal cycles. After completion of the first measurements (cycles 1 and 2), there was an 11-hour break. A second measurement (cycle 3 and 4) was performed afterwards. Results of those measurements are presented in Figs. S1 and S2.



**Fig. S1.** Dependence of Seebeck coefficient on temperature during four consecutive measurement cycles with 1.2 K/min heating/cooling rate.



**Fig. S2.** Dependence of electrical conductivity on temperature during consecutive measurement cycles with 1.2 K/min heating/cooling rate.

It can be noticed, that above the phase transition all heating and cooling measurements show similar character. The second and fourth heating data start where the previous cooling cycles finished, which is expected for measurements continuous in time. Moreover, these two heating characteristics are similar. However, the temperature dependencies differ between heating and cooling runs. Moreover, The first and third heating measurements differ from those performed immediately after cooling down. In the case of the first measurement, the Seebeck coefficient maximum and corresponding conductivity minimum are shifted towards higher temperatures. These observations indicate, that in the  $\alpha$  phase, the properties dependent not only on the temperature. The additional variable causes an increase in the Seebeck coefficient and a decrease in conductivity. The similarity of cooling dependencies obtained with different cooling rates (see. Fig. 3 in the main article) shows, that on a time scale of one measurement (cooling and heating in the  $\alpha$  phase temperature region), these changes are not influencing the results significantly. We can also conclude, that in the  $\alpha$  phase, thermal equilibrium is not reached during measurement with constant temperature changes. The material always returns to the same state after heating above the transition and cooling below this temperature.

## 2. Thermodynamic equilibrium of the transformation

The solvus lines of the Cu-Se phase diagram (in the domain of  $\delta$  instead of typical Cu:Se ratio) were approximated with polynomials  $\delta = \sum a_n T^n$ . The line between  $\alpha$  and  $\alpha+\beta$  regions was parametrized with

$$a_1 = -0.000282942300721653$$

$$a_0 = 0.116399067209279$$

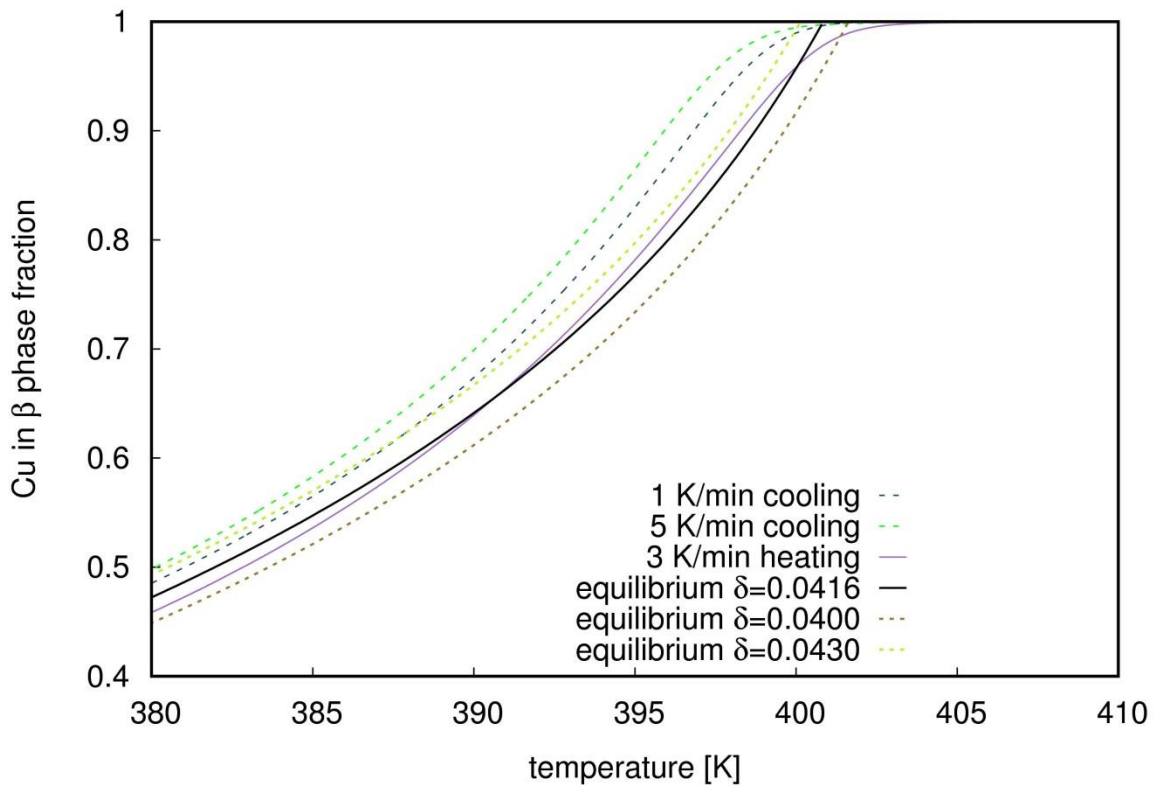
the line between  $\alpha+\beta$  and  $\beta$  with

$$a_5 = -0.000000000068303$$

$$a_4 = 0.000000122565$$

$a_3 = -0.0000878009$   
 $a_2 = 0.031383555$   
 $a_1 = -5.598238399$   
 $a_0 = 398.9861688$

Fig. S3 shows the transformation progress for 1 and 5 K/min cooling runs, 3 K/min heating run and equilibrium composition of the material for different non-stoichiometry values  $\delta$ . The 3 K/min heating curve is closest to the cooling measurements. Consequently, it should be closest to the equilibrium. For the selected  $\delta=0.0416$ , the phase transformation during the 3 K/min run shows greater progress than it would be expected from the equilibrium. However, when  $\delta=0.043$  is taken to avoid this, the onset temperature of the transition is lower than the actual found in the cooling DSC runs. On the other hand, for  $\delta=0.04$ , the difference between 3 K/min heating results and the equilibrium (in the unexpected direction) is comparable with differences between the two cooling runs, making this  $\delta$  value unreliable. Having these in mind, we decided to choose the non-stoichiometry value of 0.0416.

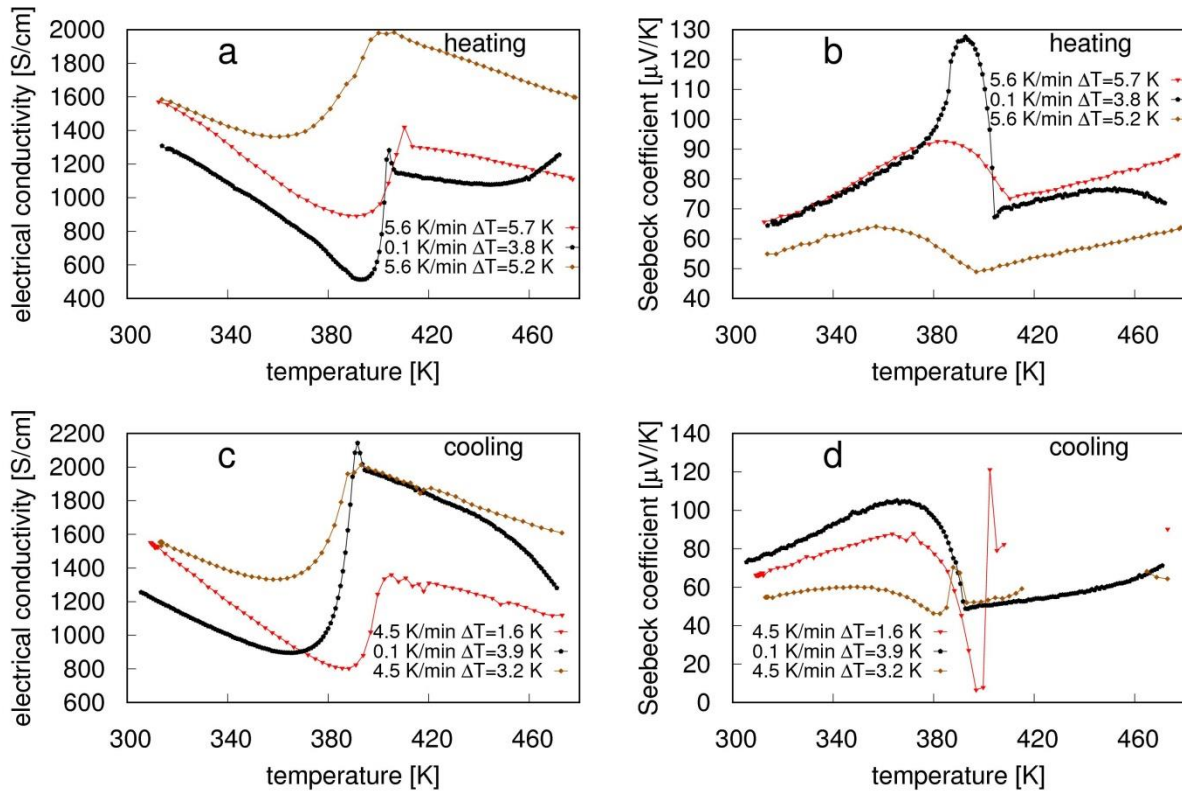


**Fig. S3.** Equilibrium fraction of copper in the  $\beta$  phase calculated for different non-stoichiometry  $\delta$  values, compared with values calculated from the selected DSC data measured during heating and cooling.

### 3. Additional thermoelectric measurements

An additional measurement was performed in order to measure the equilibrium thermoelectric properties (black line in Fig. S4). A Measurement was performed with a 0.1 K/min heating rate, preceded by an additional 5 K/min run. Above *ca.* 440 K the material changes its properties as a result of long-term keeping at elevated temperatures. Namely, increasing Seebeck coefficient and decreasing electrical conductivity was observed. The phase transition temperature was shifted towards lower temperatures. Therefore, the results obtained during cooling cannot be directly compared to those presented in Fig. 3 in the main article.

Further measurement was performed similarly to the fastest one presented in the main article but with **a** higher temperature difference (brown line). Comparison of the latter measurement with the quasi-stabilised one during cooling shows, that the changes that occurred in the material upon long heating are irreversible within 20 days between those measurements.

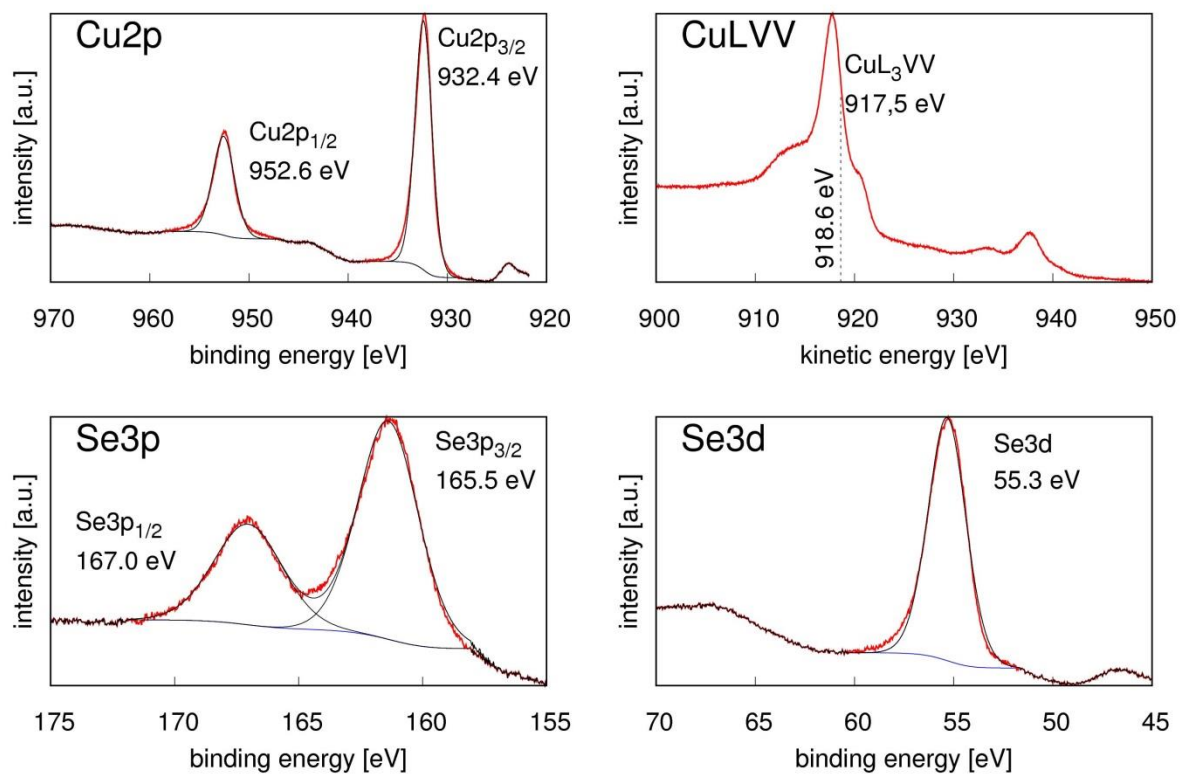


**Fig. S4.** Electrical conductivity (a, c) and Seebeck coefficient (b, d) values measured during heating (a, b) and cooling (c, d) from the fastest measurement presented in the main article (red), the quasi-stabilised measurement (black) and the measurement with a higher temperature gradient (brown). The order of the cycles is given by the key (top to bottom). Rates given in the key are actual measured values. Values of the temperature difference between electrodes for the local minimum of the Seebeck coefficient during the transition. In panel d, some Seebeck coefficient values above 408 K are deleted due to temperature difference below 0.9 K.

The transformation of the material resulting from keeping the sample above 440 K increases the conductivity and decreases the thermopower. This is characteristic of higher copper deficiency. Indeed, the EDX composition analysis performed after all electrical measurements showed  $\text{Cu}_{1.92\pm 0.27}\text{Se}$  composition. Comparison of the transition temperature and the phase diagram suggests composition close to  $\text{Cu}_{1.94}\text{Se}$ .

#### 4. XPS measurements

XPS analysis of the material was carried out on the sample on which the electrical measurements were previously performed. The binding energies were corrected using the background C1s line (285.0 eV) as a reference. The spectra were analysed using a Shirley background subtraction and Gaussian-Lorentzian curve. Different regions of the spectrum are presented in Fig. S5.



**Fig. S5.** Selected regions of the XPS spectrum with fitted peak positions. The 918.6 eV kinetic energy value marked with a dashed line on the CuLVV plot corresponds to the peak position expected for metallic Cu.