

## Supplementary Information

### Structural relaxation in layered, non-stoichiometric Fe<sub>7</sub>S<sub>8</sub>

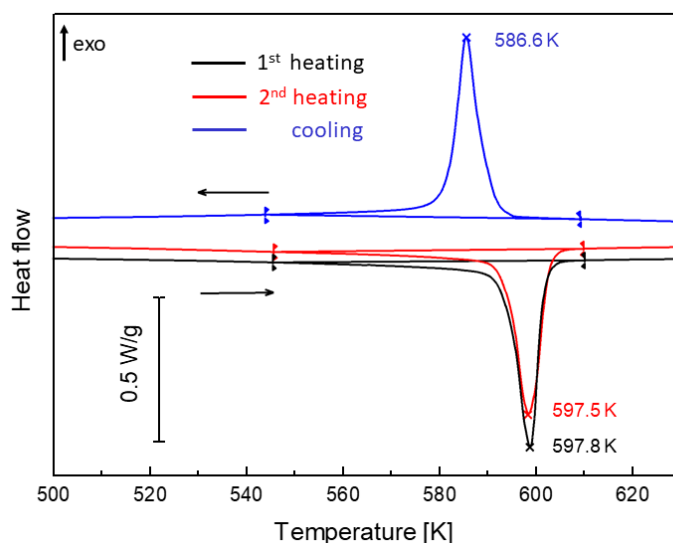
D. Koulialias<sup>a,b</sup>, J. E. K. Schawe<sup>c</sup>, J. F. Löffler<sup>b</sup>, and A. U. Gehring<sup>a</sup>

<sup>a</sup>*Institute of Geophysics, Department of Earth Sciences, ETH Zurich, 8092 Zurich, Switzerland*

<sup>b</sup>*Laboratory of Metal Physics and Technology, Department of Materials, ETH Zurich, 8093 Zurich, Switzerland*

<sup>c</sup>*Mettler-Toledo GmbH, Analytical, 8606 Nänikon, Switzerland*

#### Correction of the DSC curve and determination of the apparent transformation enthalpy



**Fig. S1:** DSC curves obtained from an Fe<sub>7</sub>S<sub>8</sub> single crystal (19.26 mg) repeatedly measured at  $\pm 10$  K/min.

The DSC curves of a single crystal in Fig. S1 illustrate the weak first-order  $\beta$ -transformation. The transformation temperature is related to the peak temperature at 597.8 K during the first heating measurement. During cooling, the transformation occurs at 586.6 K with relevant supercooling. The second heating measurement exhibits the transformation at nearly the same temperature (597.5 K) as during the first heating.

For the correct determination of the transformation temperature, one needs to consider that the heat-transfer path in the DSC influences the curve shape. For heat-flux DSC, this influence is well known and discussed elsewhere (e.g. [S1]).

Assuming a perfectly symmetric DSC cell, the heat flow curve,  $\Phi(T_p)$ , is determined in a first approximation by:

$$\Phi(T_p) = k \Delta T_{RS}, \quad (S1)$$

where  $T_p$  is the program temperature,  $k$  is a calibration factor that depends on the internal thermal resistances of the DSC cell and crucible, and  $\Delta T_{RS}$  is the temperature difference between the reference and sample side. This equation is typically used in heat-flux DSC and perfectly holds for a symmetric calorimeter at steady-state conditions with  $T_p = T_R$  ( $T_R$  is the reference temperature) and sufficiently small  $\Delta T_{RS}$ .

During a thermal event, a peak occurs in the DSC curve and the sample temperature  $T_S$  differs significantly from  $T_R$ . The heat flow due to the transformation is  $\Phi_t = \Delta H_t d\alpha/dt$ , where  $\Delta H_t$  is the enthalpy of the transformation and  $\alpha$  is the extent of transformation. According to Ref. [S1] it follows for an ideally symmetric calorimeter:

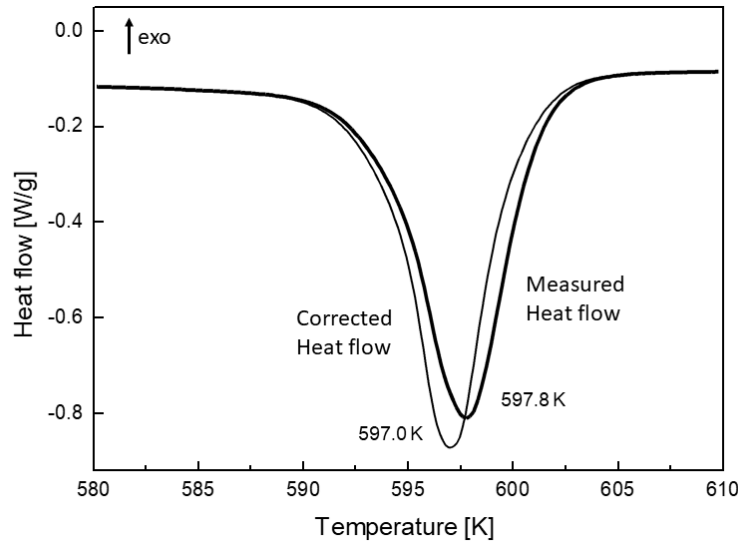
$$\Phi = \Phi_t + C_s \beta = k \Delta T_{RS} + C \frac{dT_{RS}}{dt} + C_s \frac{dT_S}{dt}, \quad (S2)$$

where  $C$  is the effective heat capacity of both the sample and the reference side of the DSC and  $C_s$  is the heat capacity of the sample.

Taking  $\frac{dT_S}{dt} = \beta - \frac{dT_{RS}}{dt}$ ,  $\frac{dT_{RS}}{dt} = \beta \frac{dT_{RS}}{dT_R}$  and  $C \approx C - C_s$ , eq. (S2) leads to

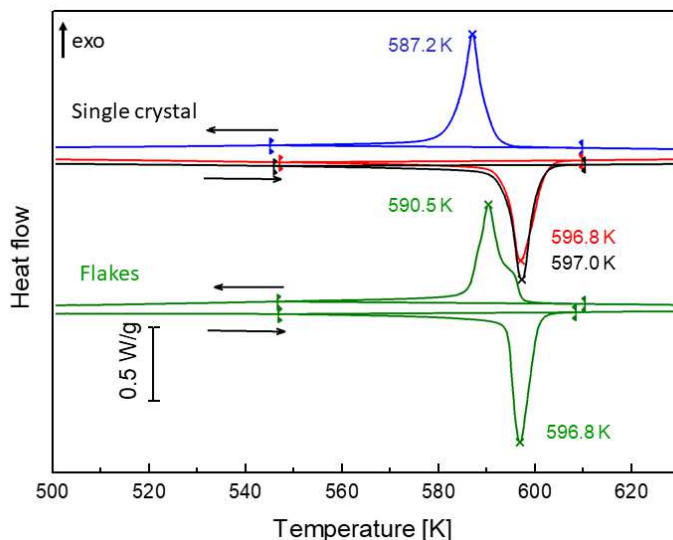
$$\Phi_t = k \Delta T_{RS} + C \beta \frac{dT_{RS}}{dT_R}. \quad (S3)$$

This equation is employed to correct the shape of the DSC peaks by its first derivative. With the parameters  $k$  and  $C$  determined by calibration, the correction can be performed with the DSC software and is named “desmearing”. Figure S2 displays the effect of this correction on the peak shape of the first heating curve shown in Fig. S1. The peak intensity increases slightly and the peak temperature shifts by 0.8 K. The corrected peak marks the temperature of the  $\beta$ -transformation.



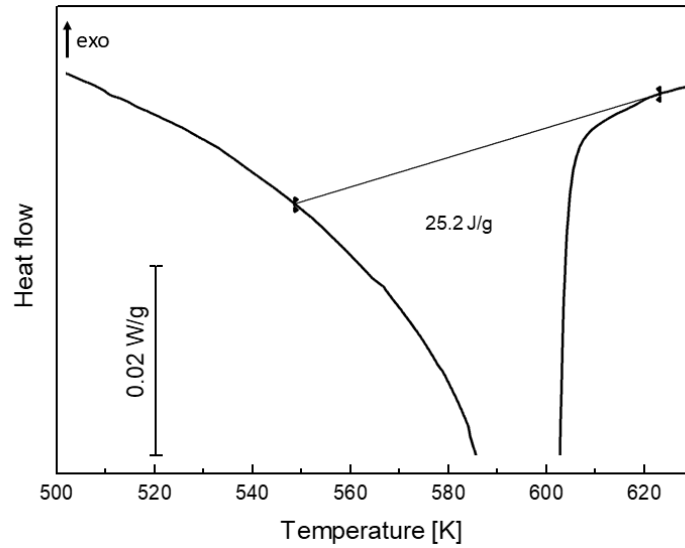
**Fig. S2:**  $\beta$ -transformation of an  $\text{Fe}_7\text{S}_8$  single crystal. The bold curve is the original DSC curve, whereas the other is corrected according to eq. (S3).

Figure S3 compares the corrected DSC curves obtained from a single crystal with those of a sample consisting of several flakes. It is worth noting that for FDSC measurements single flakes were used. The shift of 0.2 K in the second run for the single crystal indicates a slight decrease of the cation ordering in the 4C structure. Moreover, the transformation of the single crystal reveals supercooling, as indicated by the difference of 9.8 K between the heating and cooling peaks. Compared to the single crystal, the flakes reveal upon heating a decreased transformation temperature of 0.2 K and upon cooling a supercooling of 6.3 K. These different properties are most likely due to particle-size effects.



**Fig. S3:** Heat flow curves plotted versus sample temperature. The upper curves are those of Fig. S1 after correction (“desmearing”). The corrected curves of an assembly of flakes (8.45 mg) are shown in green.

The  $\beta$ -transformation is of weak first order with a configurational heat-capacity contribution and a latent heat component. To illustrate the determination of the transformation enthalpy, Fig. S4 shows in high magnification the measured transformation of the single crystal (Fig. S3). The baseline, corresponding to a linear extrapolation of the measured curve above 620 K, is an approximation to determine the apparent latent transformation enthalpy, which is 25.2 J/g for the single crystal.



**Fig. S4:** Magnified transformation peak from the first heating curve of the single crystal displayed in Fig. S3, including the baseline for the approximate determination of the apparent latent transformation enthalpy.

### References

- [S1] G.W.H. Höhne, Problems with the calibration of differential scanning calorimeters, *Thermochim. Acta*, 1982, **69**, 175-197.
- [S2] K.-H. Illers, Die Ermittlung des Schmelzpunktes von kristallinen Polymeren mittels Wärmeflusskalorimetrie (DSC), *Eur. Polym. J.*, 1974, **10**, 911-916.