Online STK Meeting
2020

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Determination of Thermodynamic Properties of Polymorphic Systems with Fast Crystallization Kinetics

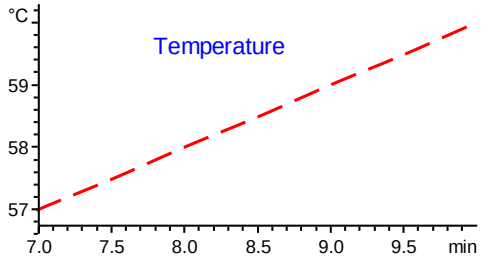
METTLER TOLEDO

Agenda

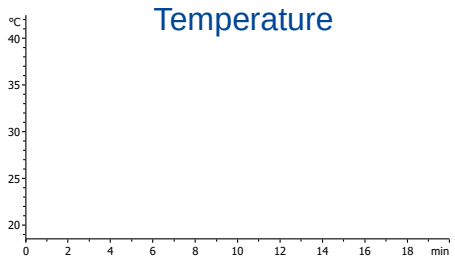
1. Experimental Techniques
2. Polymorphism
3. Metallic Glass
4. Polymorphism in BMG Forming Alloys
5. Summary

DSC 3+ with TOPEM

Different TMDSC techniques



periodic (single frequency) modulation



TOPEM® stochastic modulation

Heat Flow = Heat Capacity Component + Latent Component

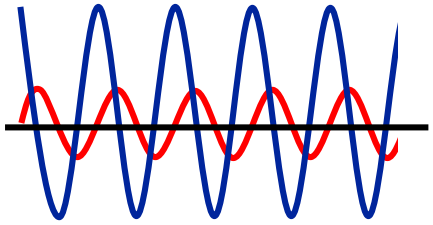
Total Heat Flow

Reversing Heat Flow — **highly sensitive to temperature change**

Non-reversing Heat Flow — **less sensitive to temperature change**

This correspondence requires quasi static conditions

TMDSC evaluation



Conventional TMDSC evaluation

average → total heat flow

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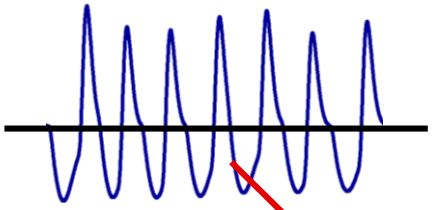
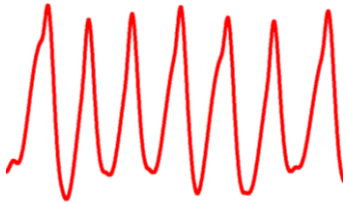
amplitude, phase shift → reversing heat flow

non-reversing heat flow





TOPEM® evaluation

not correlated component → non-reversing heat flow

\+

correlated component → reversing heat flow

average ← total heat flow

consistency check

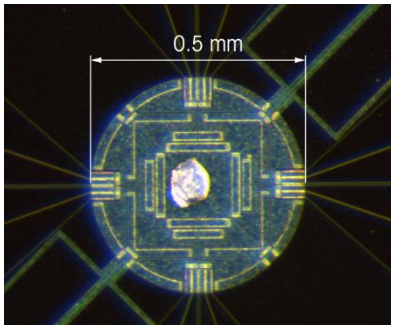
TOPEM advantages

- Stochastik modulation
  - Quasi-static heat capacity
  - Multi frequency evaluation
- Advanced evaluation procedure
  - Smaller amplitudes are possible (acurate results)
  - Use of higher heating rates
  - No blank and calibration curves required
  - Most accurate specific heat capacity in DSC
  - Consistency check

Flash DSC 2+

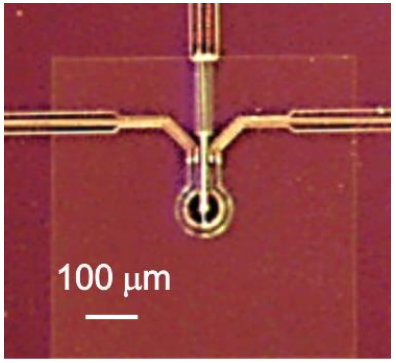
Sensor UFS1: -95 °C .. 520 °C

- Typical heating rates: 0.1 .. 20,000 K/s
- Typical cooling rates: 0.1 .. 4,000 K/s



Sensor UFH1: -95 °C..1000 °C

- Typical heating rates: 0.1 .. 60,000 K/s
- Typical cooling rates: 0.1 .. 40,000 K/s



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Polymorphism

Otto Lehmann 1877:

Physical polymer (Enantiotropy):
Transition of a stable modification in a stable modification

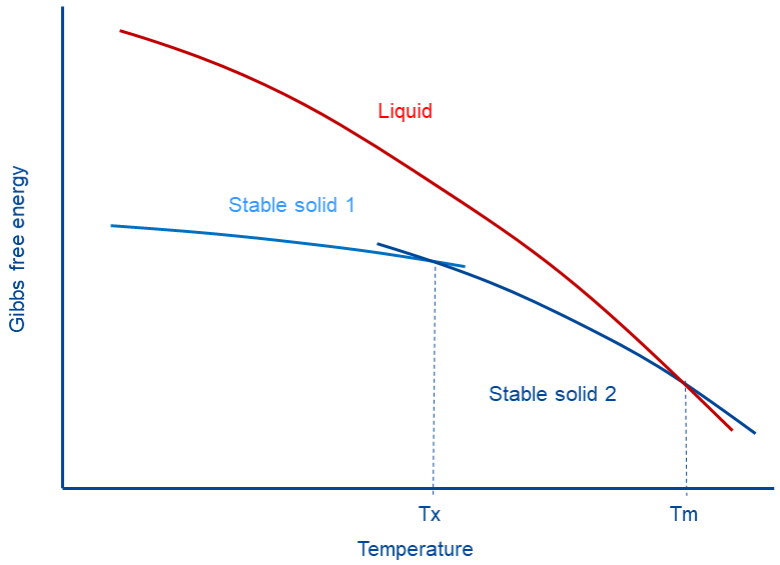
Physical metamere (Monotropy):
Possible coexistence of more modifications

Max Planck 1882: **Polymorphic phases could be in a metastable equilibrium**

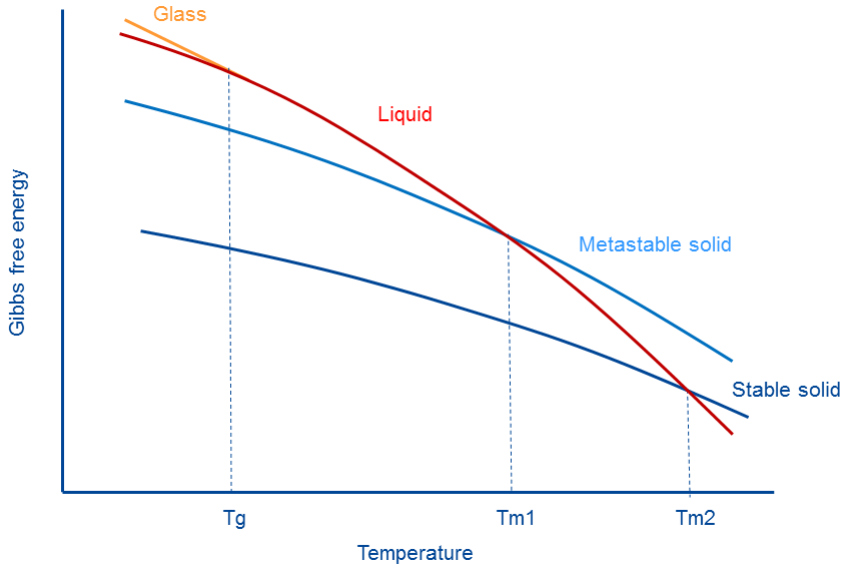
Wilhelm Ostwald 1897: **Ostwald's step rule**

Gustav Tammann 1898: **Metastable polymorphic modifications are formed at high supercooling**

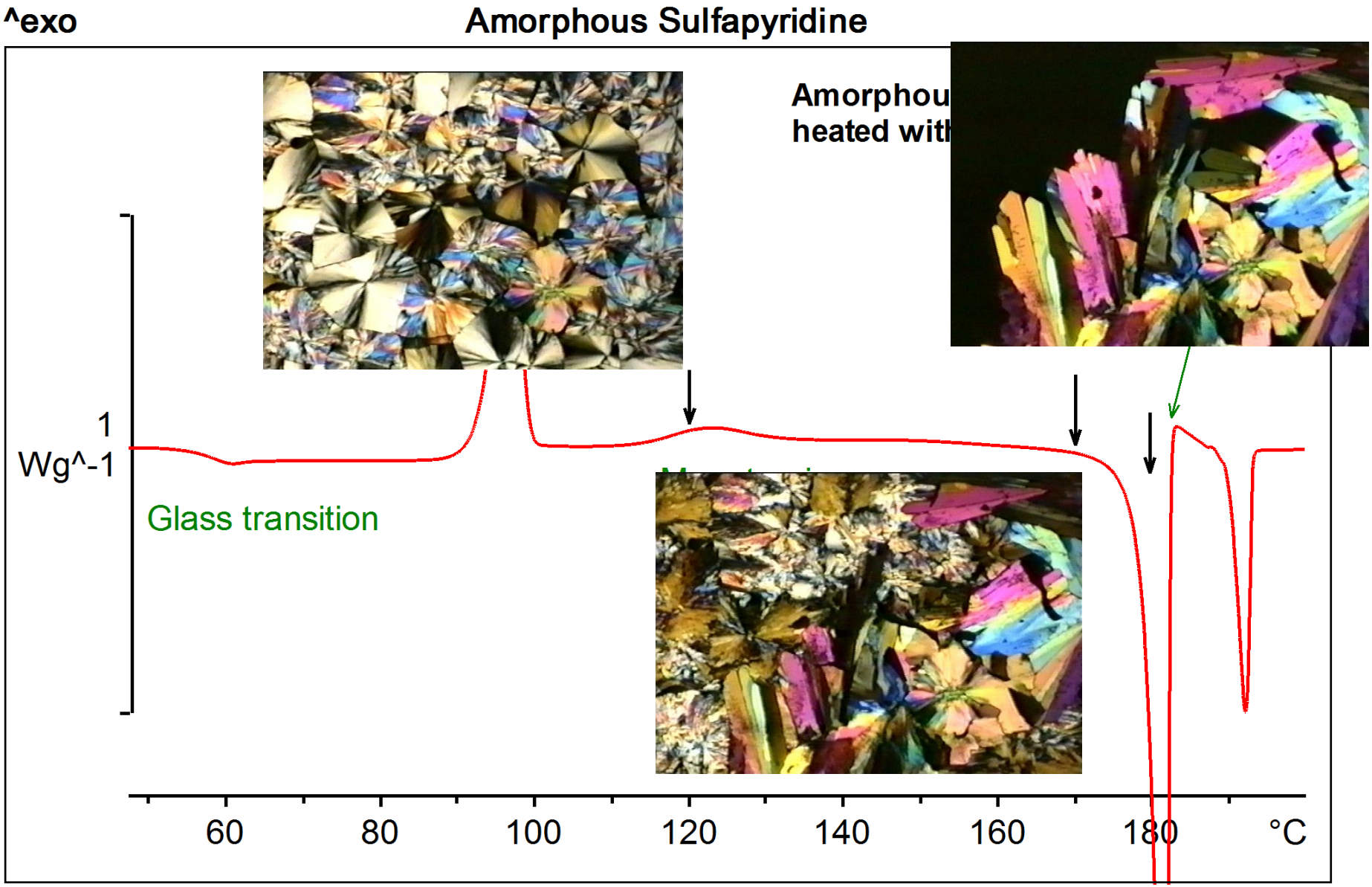
Enanzotropy



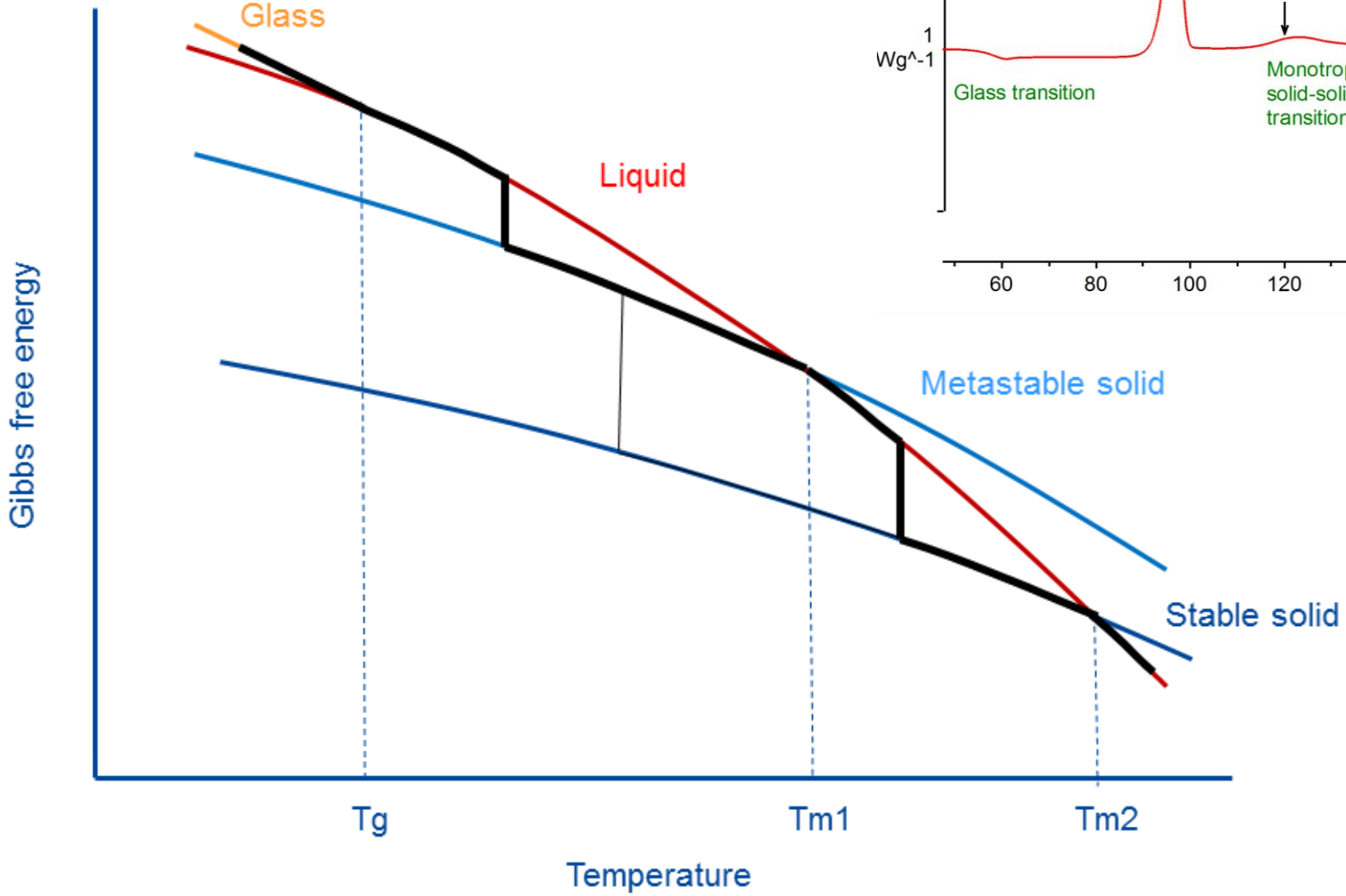
Monotropy

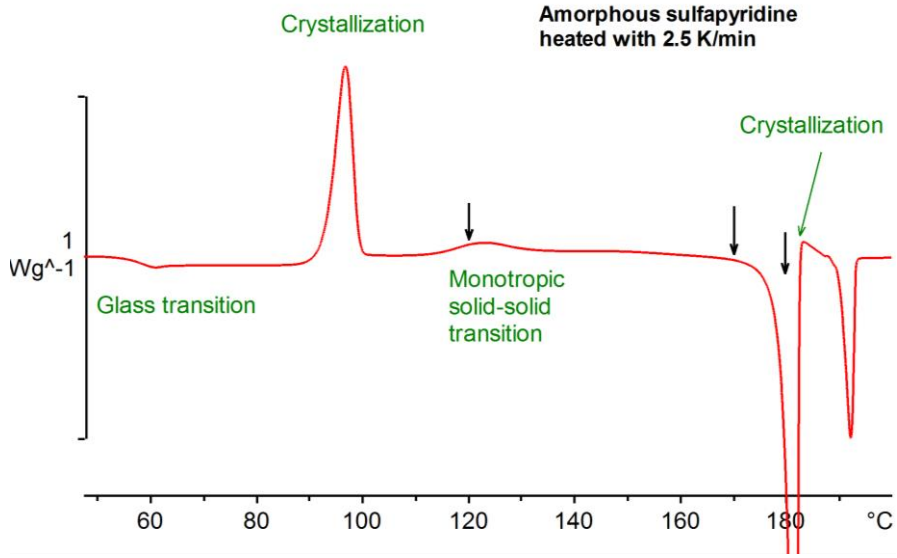


Polymorphism of Sulfapyridine



Monotropic Polymorphism





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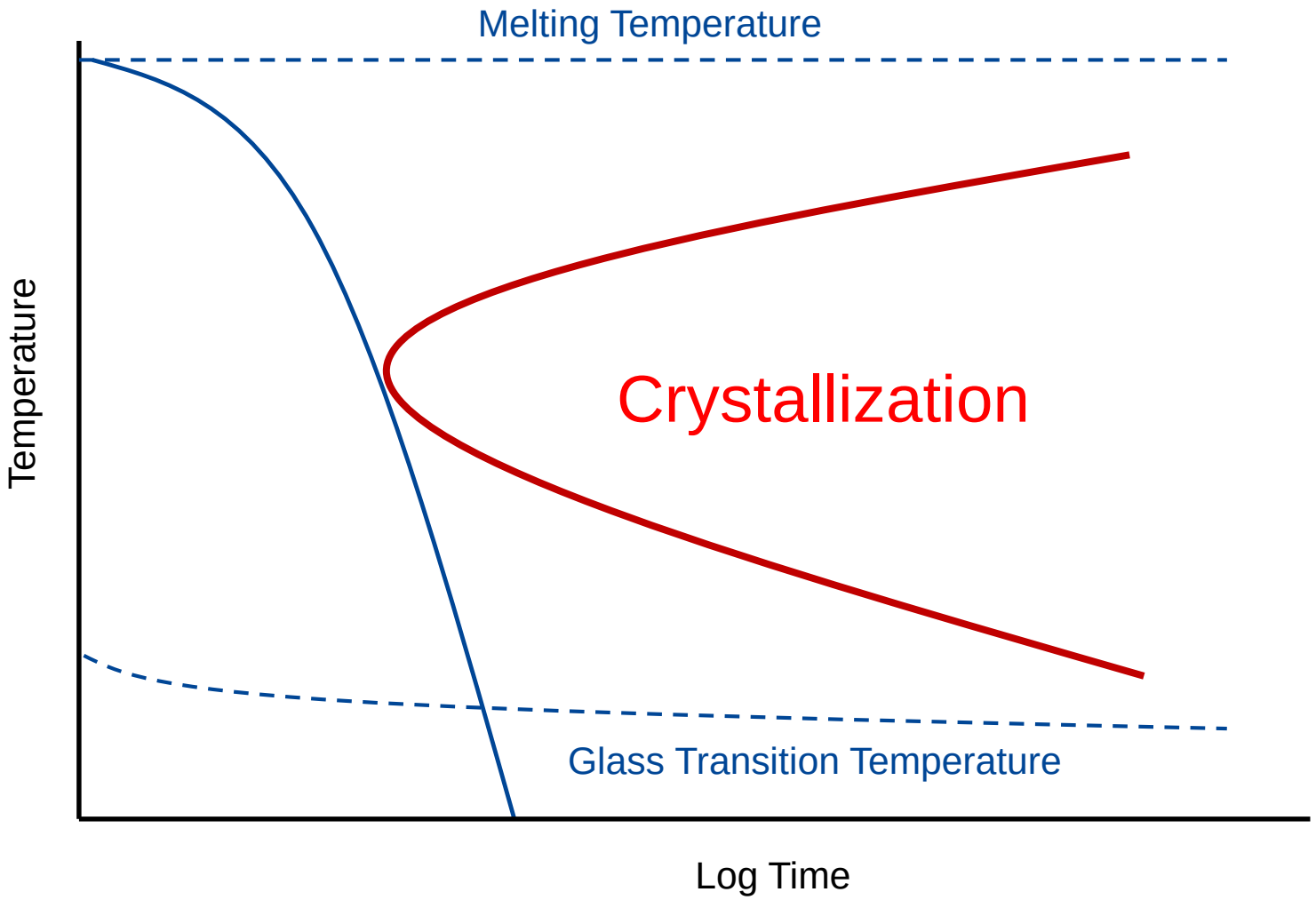
Tammann's approach to form a glass from 1903

Gustav Tammann 1903:

At sufficient fast cooling all substances can form a glass if crystallization can be bypass.



Bulk Metallic Glass

First Metallic Glass:

W. KLEMENT, JUN.
R. H. WILLENS
POL DUWEZ

Division of Engineering,
California Institute of Technology,
Pasadena, California.

Non-crystalline Structure in Solidified Gold–Silicon Alloys

No. 4740 September 3, 1960 NATURE 869

First Bulk Metallic Glass:

716 Appl. Phys. Lett. **41**(8), 15 October 1982

Bulk formation of a metallic glass: Pd_{40} Ni_{40} P_{20}

A. J. Drehman, A. L. Greer, and D. Turnbull
Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

(Received 27 May 1982; accepted for publication 30 July 1982)

Molten spheroids of Pd_{40} Ni_{40} P_{20}, of up to 0.53-cm minor diameter, were slowly cooled (1.4 K/s) on a fused silica surface under 10^{-6} Torr vacuum to a form which was entirely glassy except for some superficial crystallinity comprising less than 0.5% of the volume. The occurrence of crystallization was eliminated by subjecting the specimens to surface etching followed by a succession of heating and cooling cycles. The absence of crystallization in the bulk was confirmed by x-ray diffraction, transmission electron microscopy, and calorimetry. Using the last technique, the heat of crystallization of the glass was measured to be 5.3 ± 0.3 kJ/g atom.

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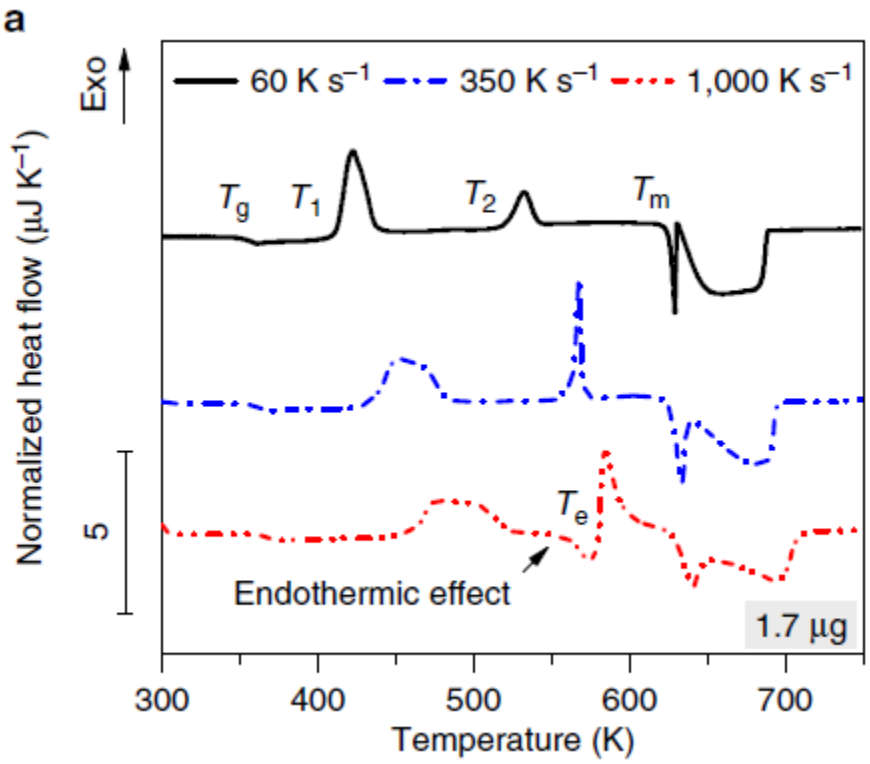
Solid–solid phase transitions via melting in metals

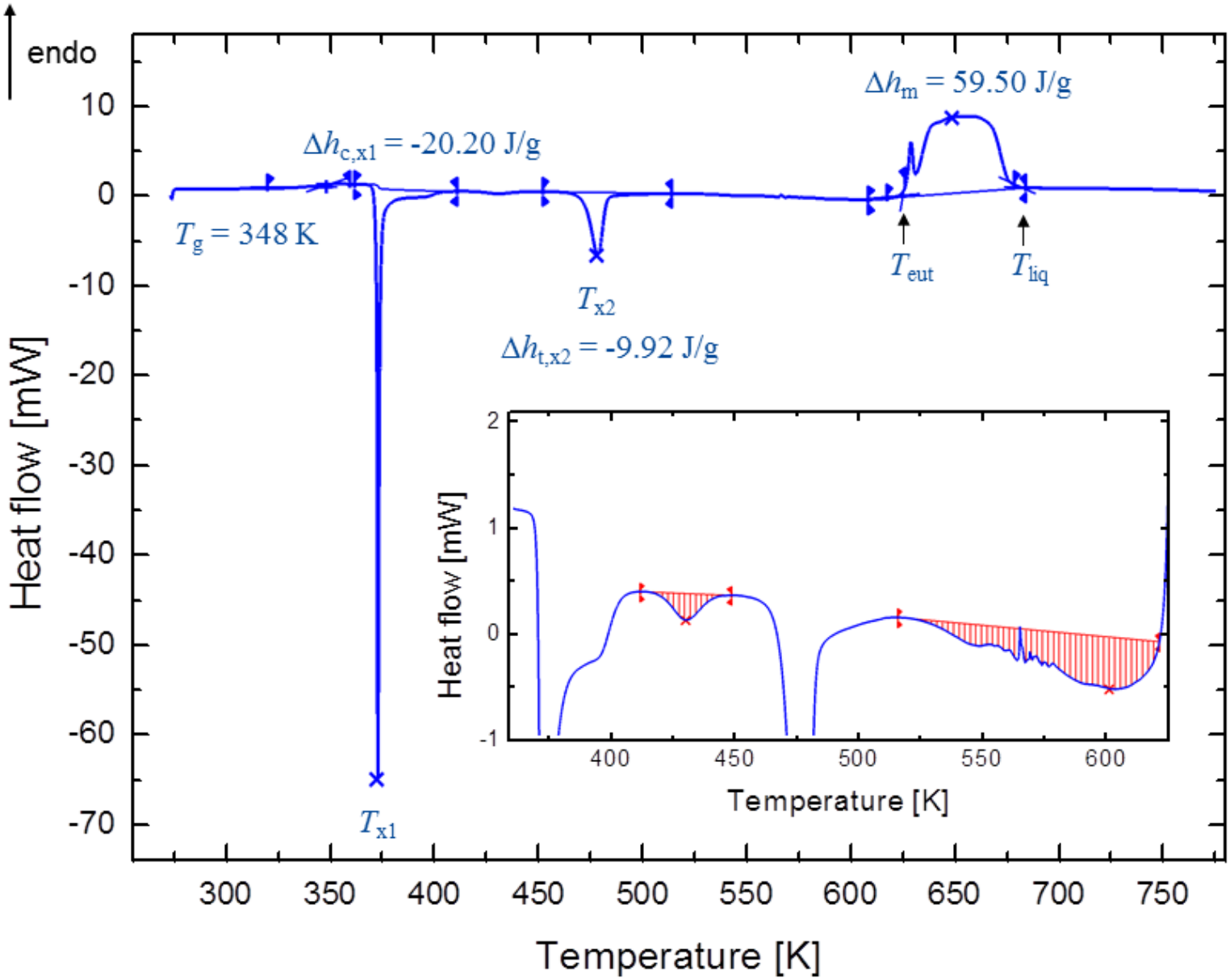
S. Pogatscher[1,2], D. Leutenegger[1], J.E.K. Schawe[3], P.J. Uggowitzer[1] & J.F. Löffler[1]

Nat. Commun. 7:11113 doi: 10.1038/ncomms11113 (2016)

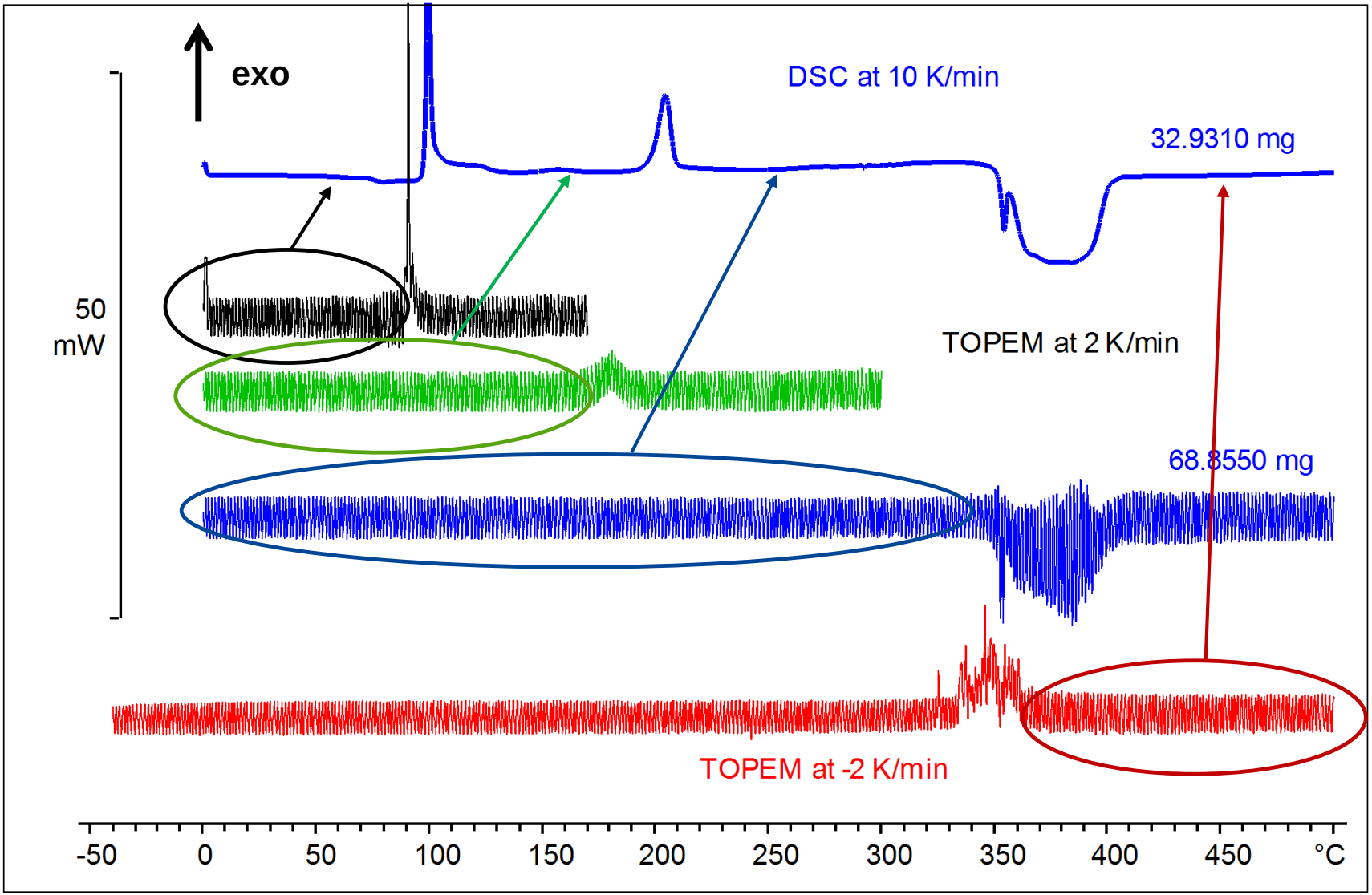
$Au_{70}Cu_{5.5}Ag_{7.5}Si_{17}$ BMG



DSC Curves and Structure



BMG: $Au_{70}Cu_{5.5}Ag_{7.5}Si_{17}$



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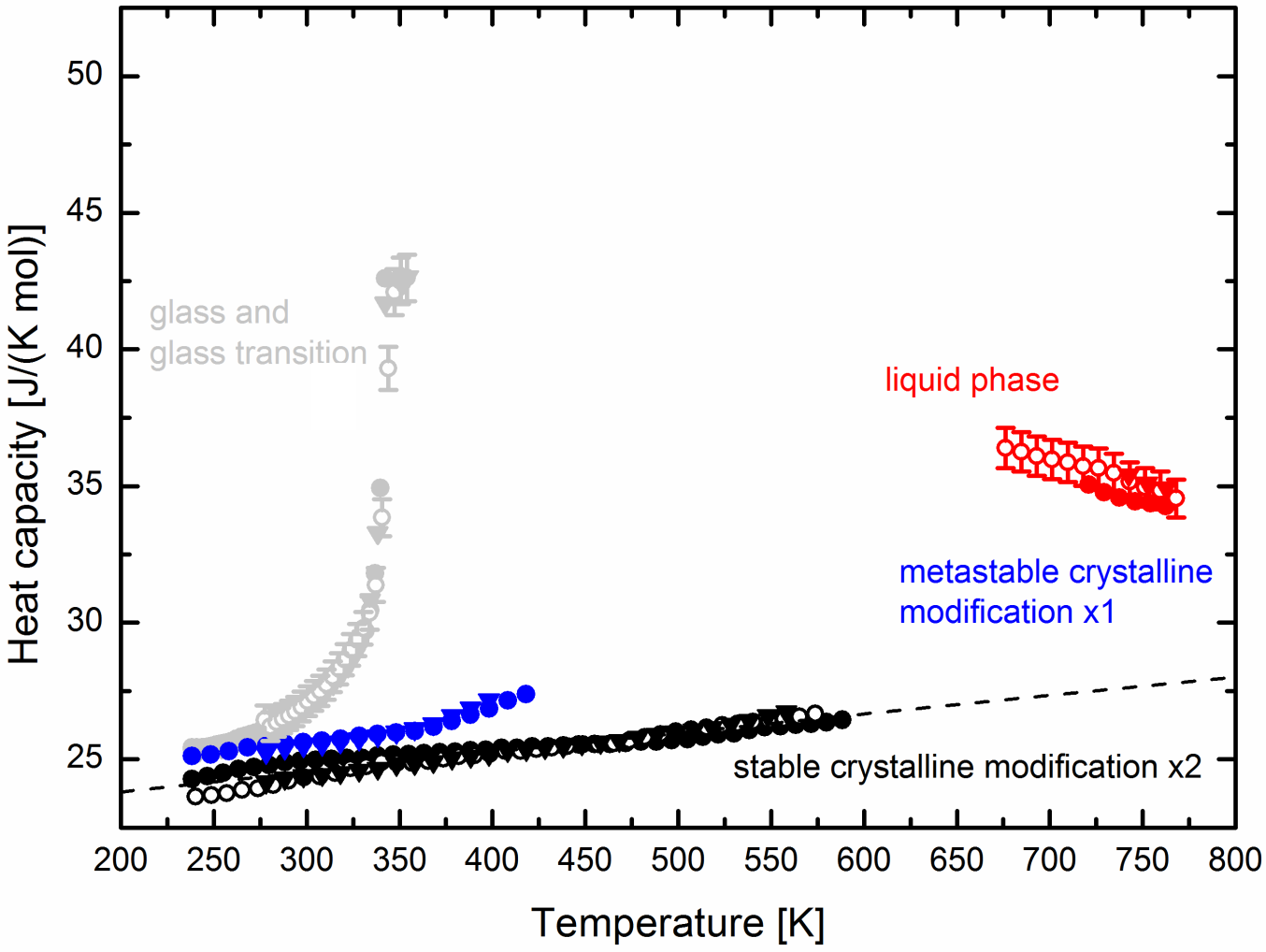


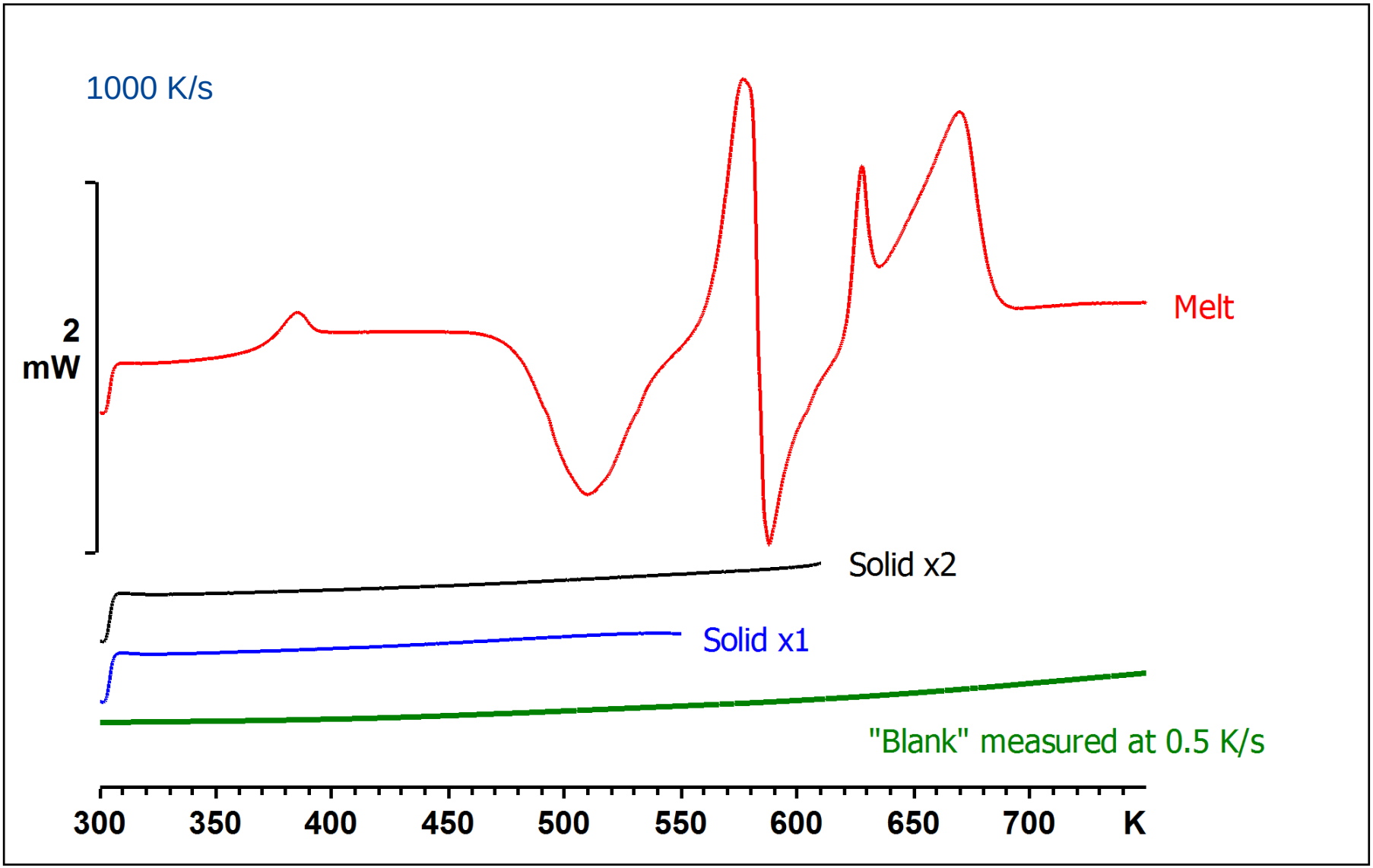
$$c_{p,\mathrm{l}}(t) = a_{\mathrm{l}} + b_{\mathrm{l}}\,T + c_{\mathrm{l}}\,T^{-2}$$

$$c_{p,\mathrm{x}}(t) = a_{\mathrm{x}} + b_{\mathrm{x}}\,T + c_{\mathrm{x}}\,T^{2}$$

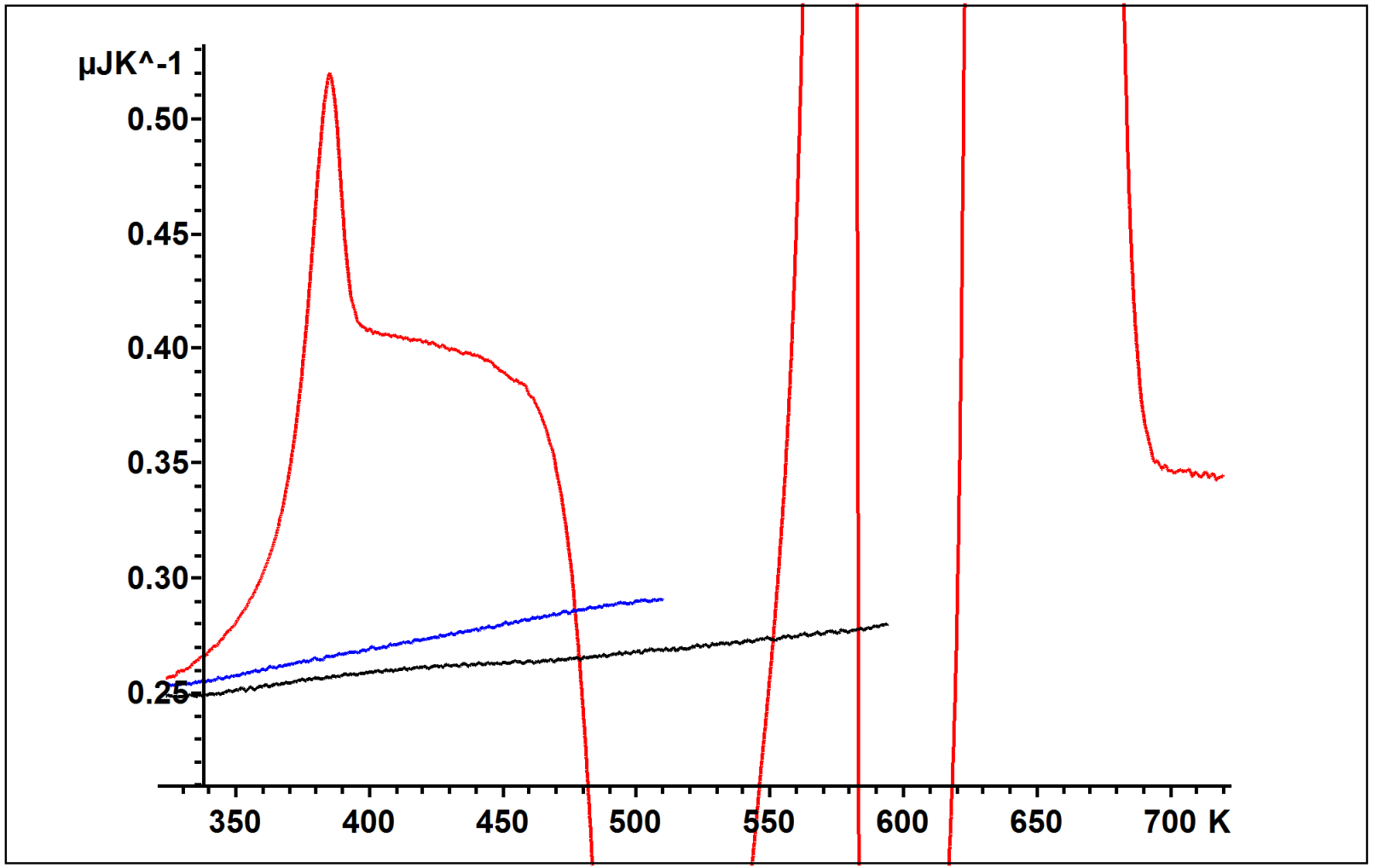
Properties of Metallic Glass

$$\Phi = m\, c_p\, \beta + \Phi_{\text{loss}}$$

C. Quick, J.E.K. Schawe, P.J. Uggowitzer, S. Pogatscher
Thermochim.Acta 677 (2019) 12-20



Properties of Metallic Glass



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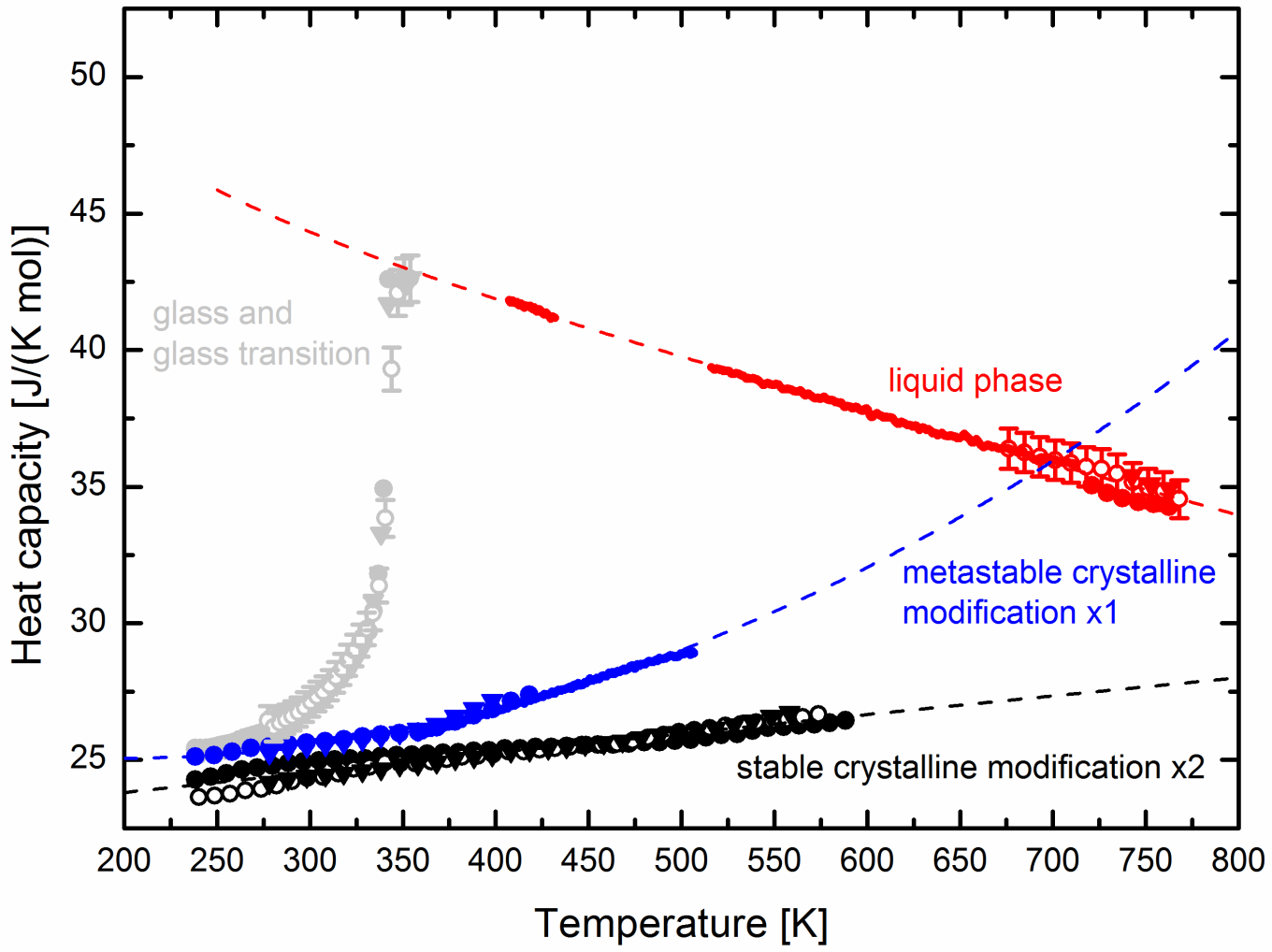


$$c_{p,\mathrm{l}}(t) = a_\mathrm{l} + b_\mathrm{l}\,T + c_\mathrm{l}\,T^{-2}$$

$$c_{p,\mathrm{x}}(t) = a_\mathrm{x} + b_\mathrm{x}\,T + c_\mathrm{x}\,T^{2}$$

Schawe, Pogatscher, Löffler, Thermochimica Acta 685 (2020) 178518

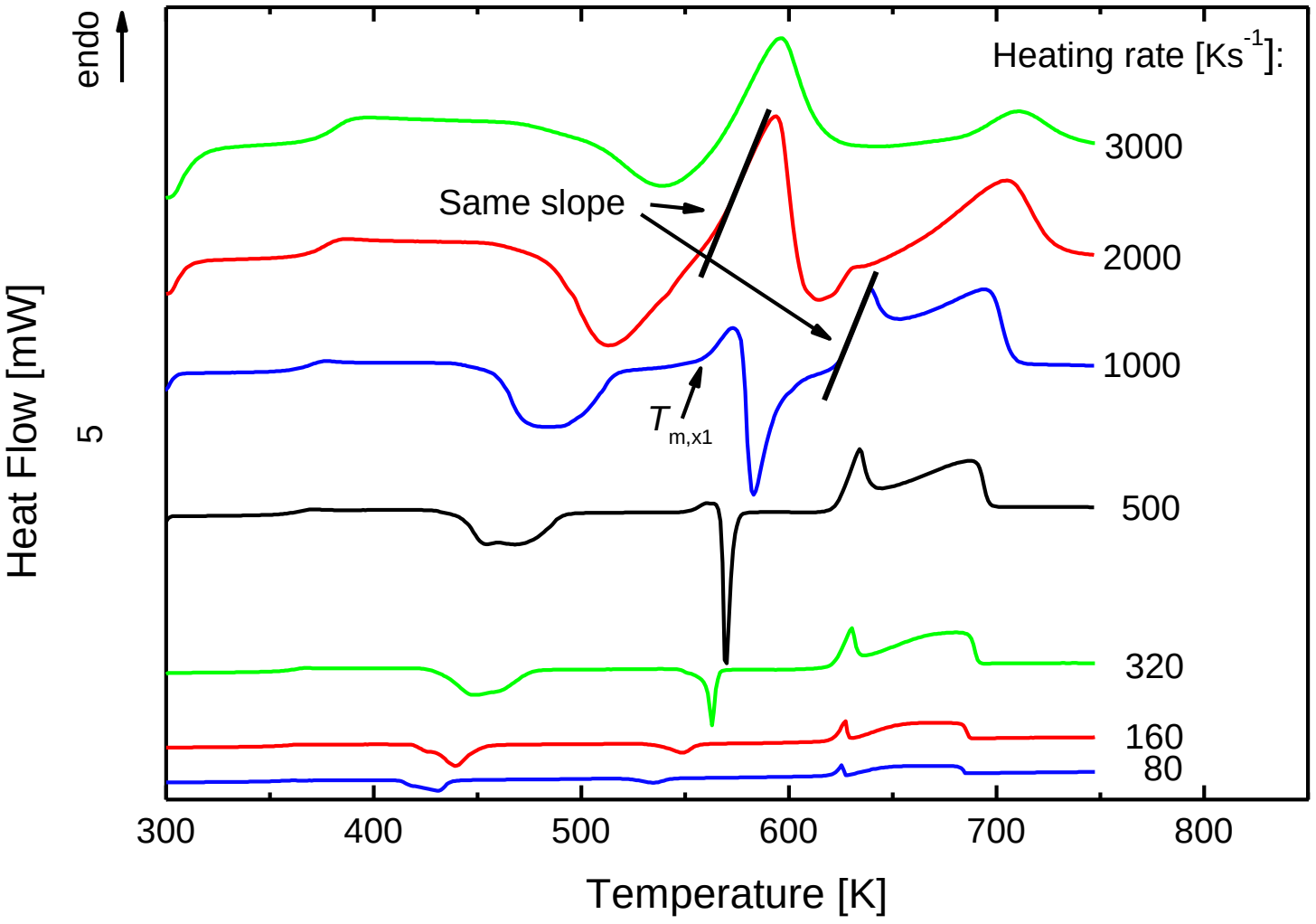
Determination of the Thermodynamic Potentials

$$\Delta h_{\mathrm{x1}}(T) = \int_{200\ \mathrm{K}}^{T} c_{p,\mathrm{x2}}\,\mathrm{d}T + \Delta h_{\mathrm{t,x2}}(T_{\mathrm{x2}}) - \int_{200\ \mathrm{K}}^{T_{\mathrm{x2}}} c_{p,\mathrm{x1}}\,\mathrm{d}T + \int_{200\ \mathrm{K}}^{T} c_{p,\mathrm{x1}}\,\mathrm{d}T$$

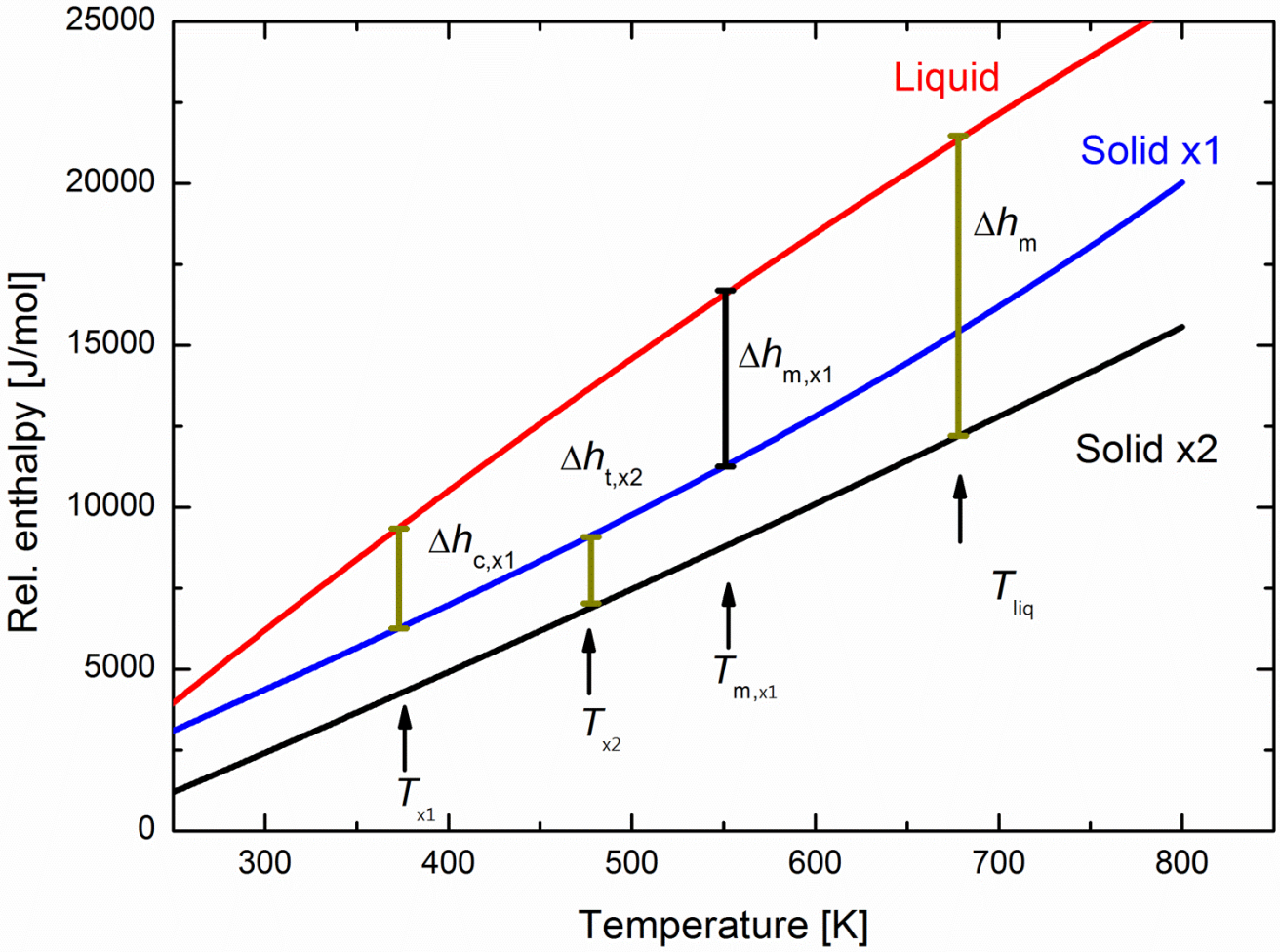
$$\Delta s_{\mathrm{x1}}(T) = \Delta s_{\mathrm{l}}(T_{\mathrm{m,x2}}) - \frac{\Delta h_{\mathrm{m,x1}}}{T_{\mathrm{m,x1}}} - \int_{200\ \mathrm{K}}^{T_{\mathrm{m,x2}}} \frac{c_{p,\mathrm{x1}}}{T}\,\mathrm{d}T + \int_{200\ \mathrm{K}}^{T} \frac{c_{p,\mathrm{x1}}}{T}\,\mathrm{d}T$$

$$\Delta g_{\mathrm{x1}}(T) = \Delta h_{\mathrm{x1}}(T) - T\Delta s_{\mathrm{x1}}(T)$$

BMG: $Au_{70}Cu_{5.5}Ag_{7.5}Si_{17}$



BMG: $Au_{70}Cu_{5.5}Ag_{7.5}Si_{17}$



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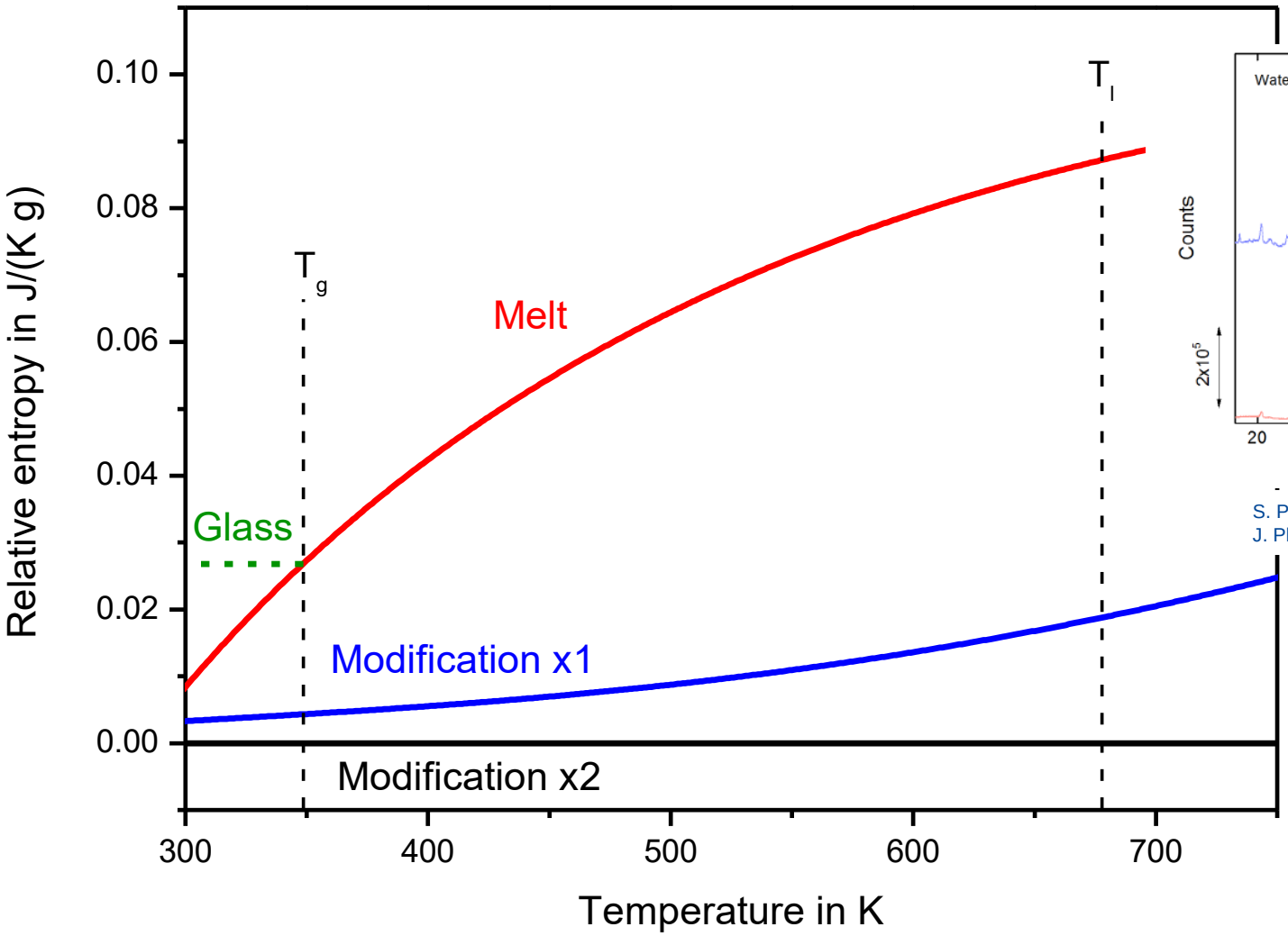
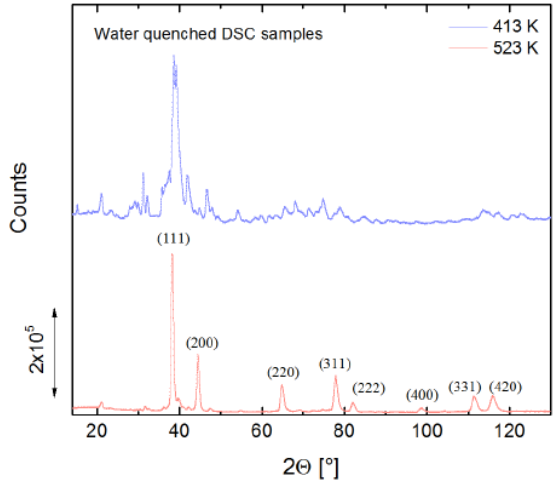
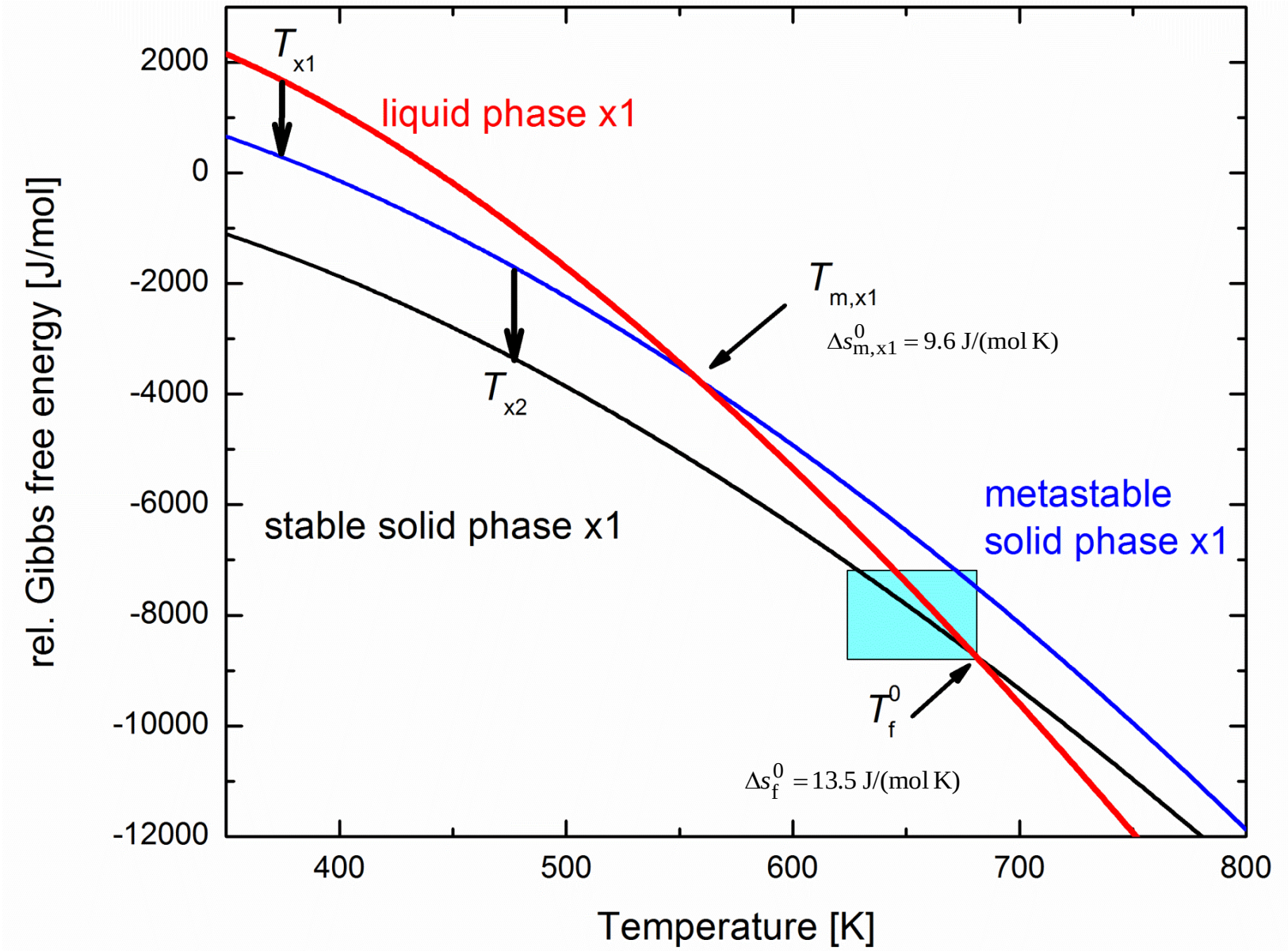


XRD patterns



S. Pogatscher at al.
J. Phys.: Condensed Matter, 30 (2018) 234002

BMG: $Au_{70}Cu_{5.5}Ag_{7.5}Si_{17}$



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Conclusion

- BMG forming alloys form metastable modifications.
- BMG forming alloys show monotropic polymorphism and follow Ostwald's step rule.
- The measurement of the heat capacity of the metastable phases are required to generate a Gibbs-free energy diagram.
- The heat capacity of the metastable phases of BMG forming alloys can be measured by TMDSC and FDSC.

Thanks to

D. Leutenegger, P. J. Uggowitzer, M. Pavithran, R. Schaeublin, C. Quick,

Stefan Pogatscher
Leoben, Austria

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