

62 years of innovation in Thermal Analysis from METTLER TOLEDO



Keith Racman

METTLER TOLEDO

METTLER TOLEDO
Thermal Analysis

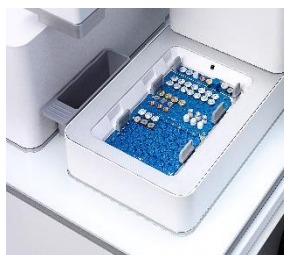


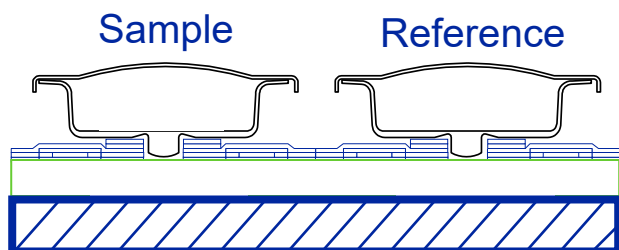
DSC 5+

The New Standard

METTLER TOLEDO

- FlexMode™, choose power compensation or heat flux mode
- Power compensation measurement mode
- MultiStar™ sensor with 136 thermocouples
- Patented electrical heat flow adjustment
- Unrivalled modular concept
- FlexCal™ adjustment and calibration
- Innovative robot with gas-purged sample chamber





DSC 3+

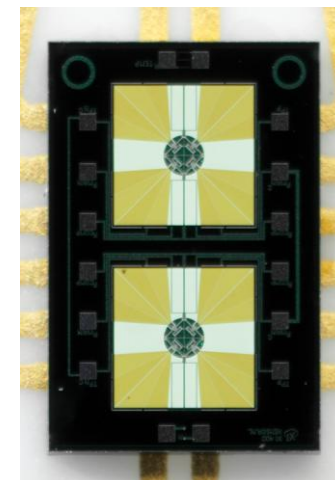
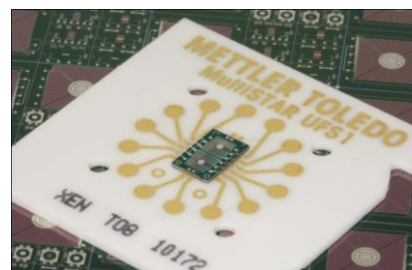


TGA/DSC 3+

Heat Flux DSC



Flash DSC 2+



Power Compensated DSC



DSC Sensor

Power Compensation and Heat Flux

- FlexMode™: Choose between power compensation and heat flux mode depending on measurement requirements.
- Power compensation mode has a very short signal-time constant, providing excellent resolution and therefore the ability to separate close-lying thermal effects.
- Heat flux mode has extremely low levels of noise which provides the highest sensitivity for the detection of weak effects or transitions.

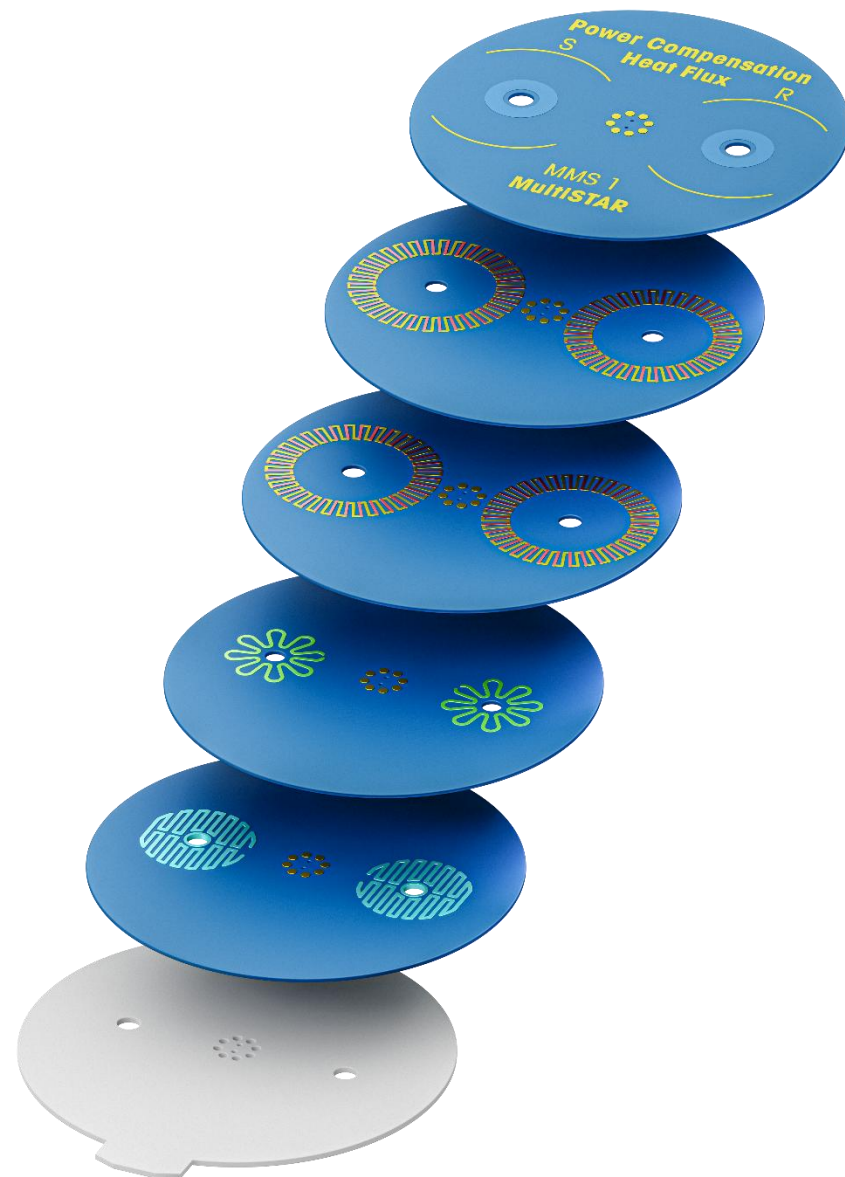


The robust, chemically-resistant, ceramic surface of the sensor means that measurements can be run at high temperatures and in aggressive atmospheres without any risk of corrosion.

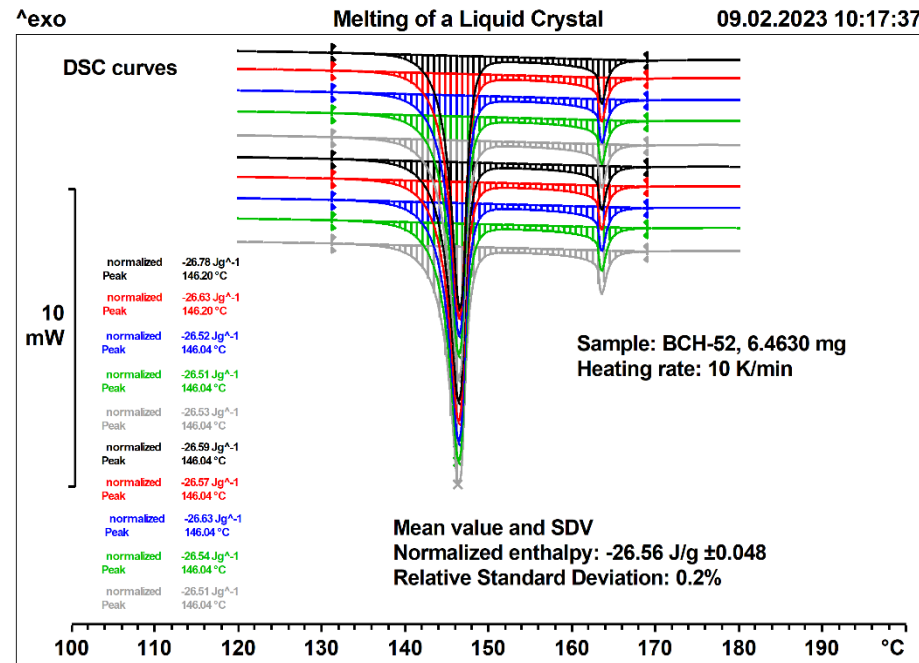
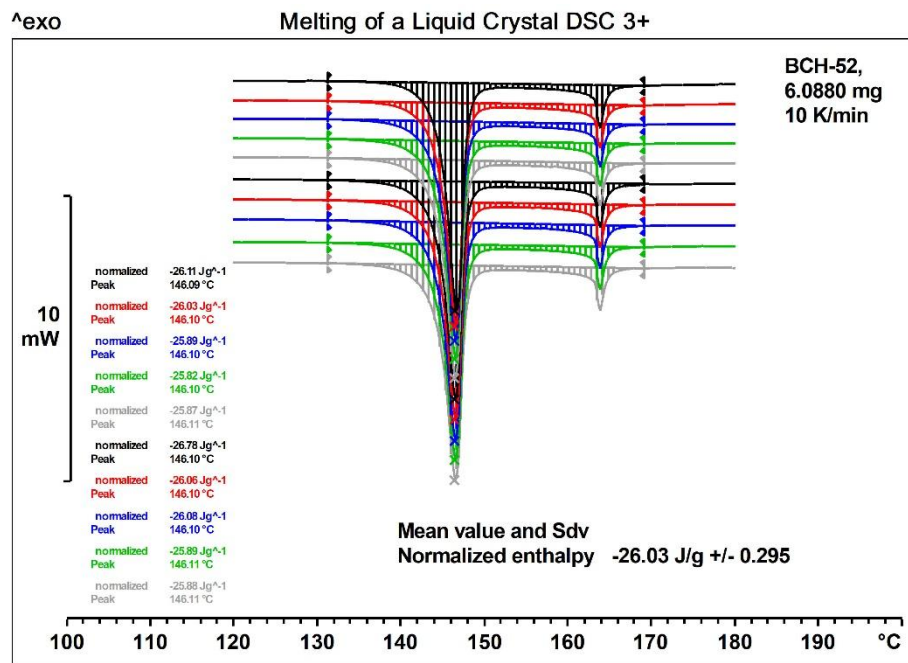
DSC Sensor

Power Compensation and Heat Flux

- The innovative multi-layer design of the MMS 1 sensor includes:
 - 136 thermocouples in 2 layers to measure the heat flow (Au/AuPd)
 - 2 heaters for power compensation
 - Absolute sample and reference temperature sensors

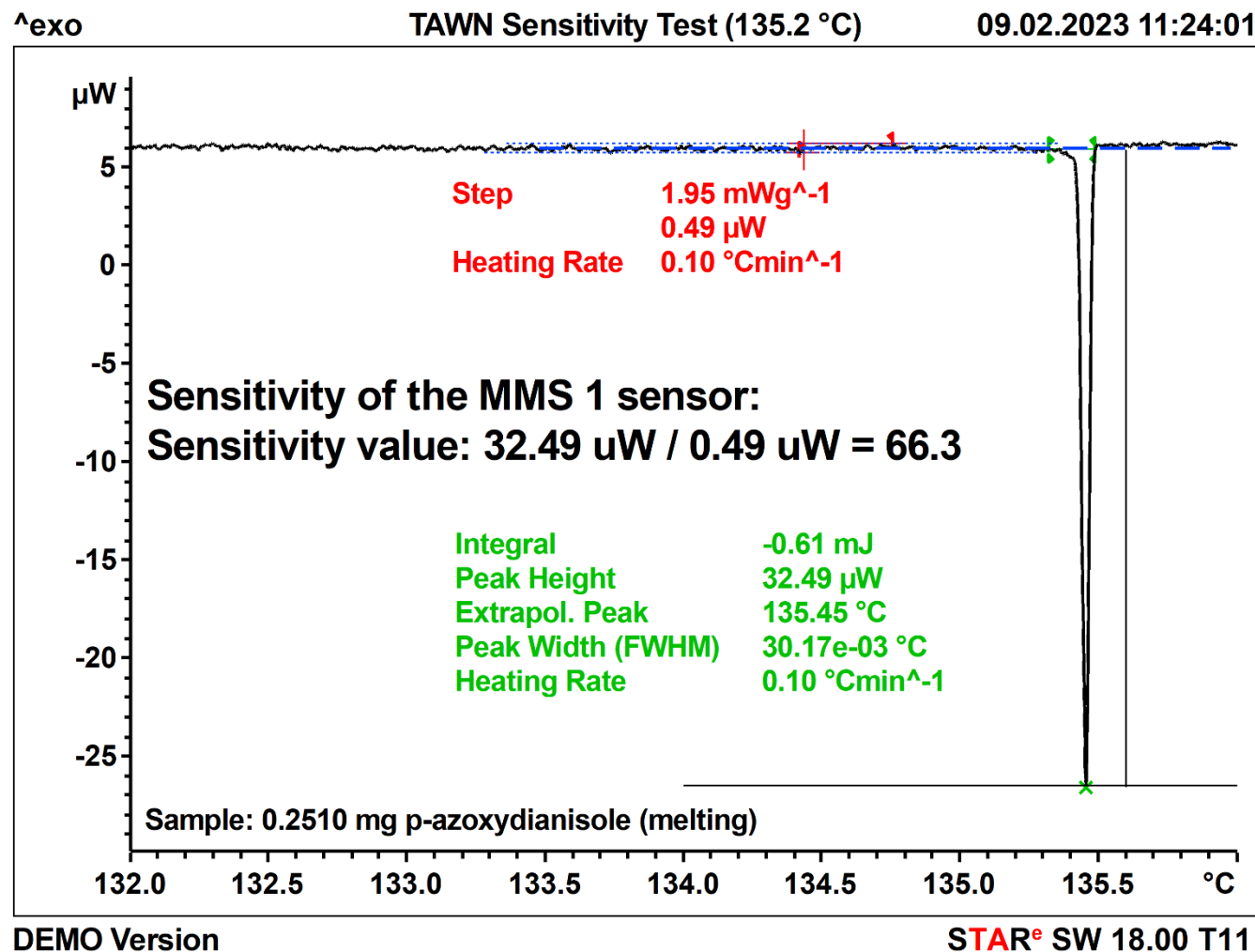


Enthalpy reproducibility - DSC 3+: 1.1%; DSC 5+: <0.2%



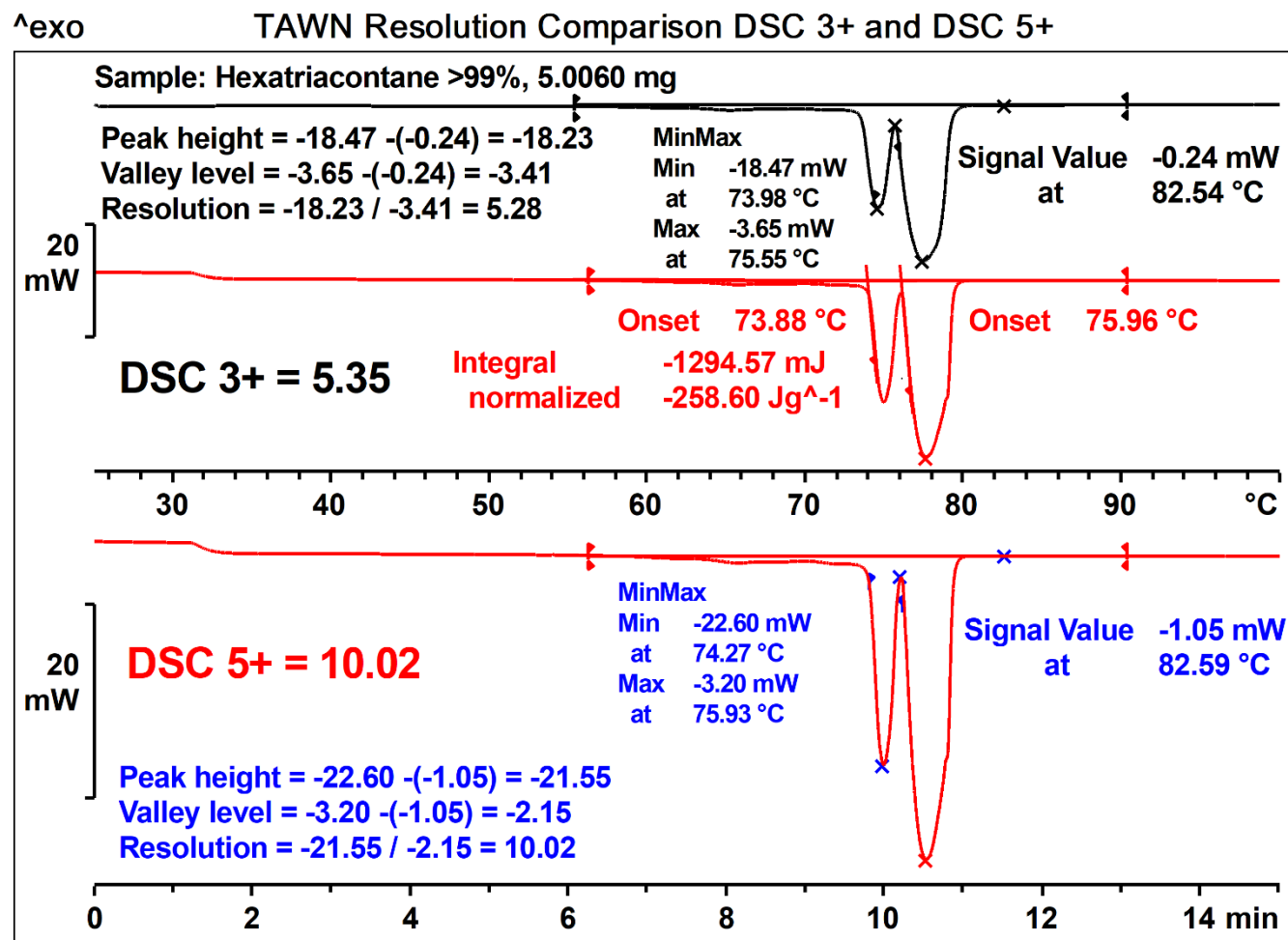
- Polymorphy studies in pharma need a high enthalpy reproducibility.
- Important to achieve that:
 - optimal furnace lid construction (avoid thermal leakages)
 - excellent placing precision (sample changer, diameter MultiStar)
 - best thermal contact pan to sensor (cleaning)

DSC 5+ has even a 18% higher sensitivity than DSC 3+ with HSS sensor.



A Better DSC: TAWN Resolution DSC 3+ and 5+ Results

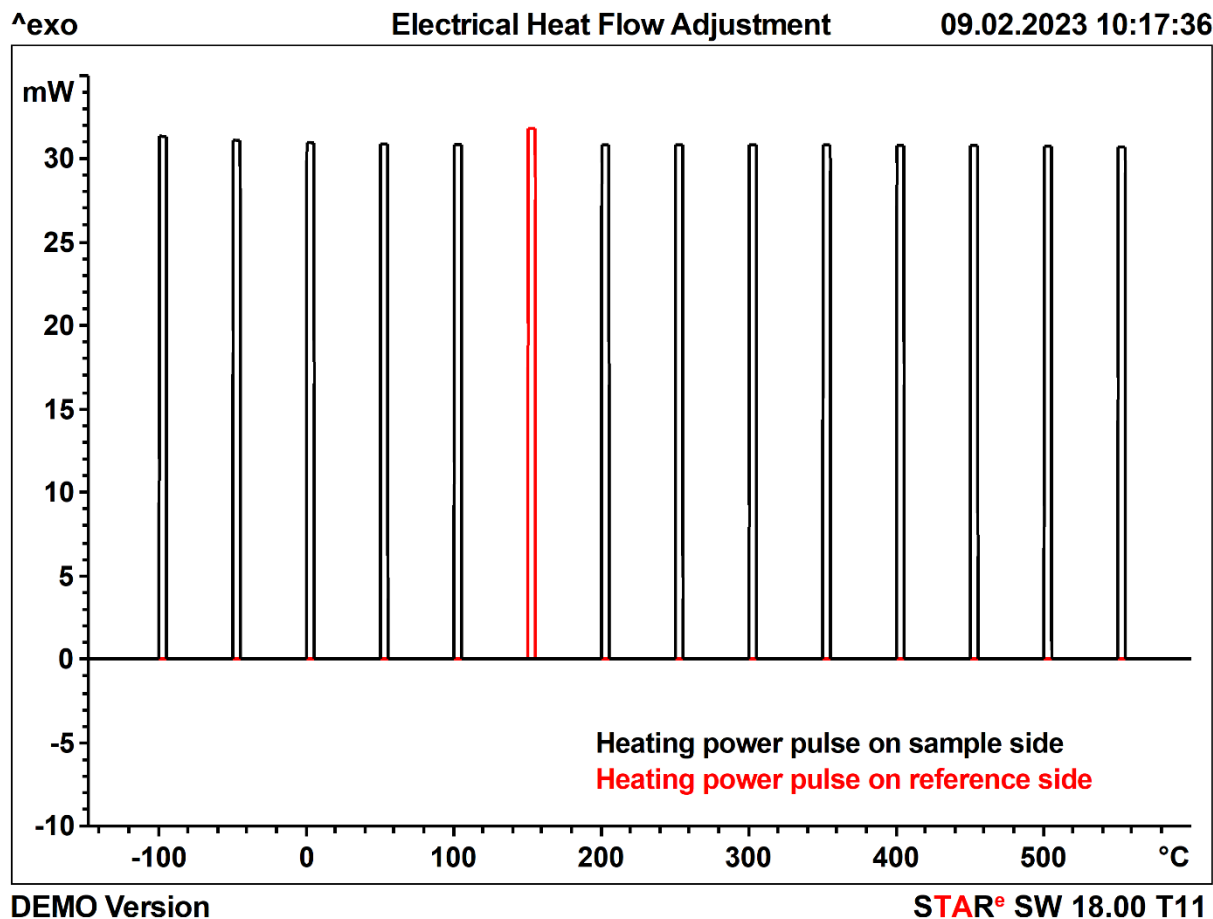
Factor 2 better



DEMO Version

STAR^e SW 18.00 T11

Pulses every 50 K, benefits: whole temperature range accessible, no sample preaparation, no operator bias

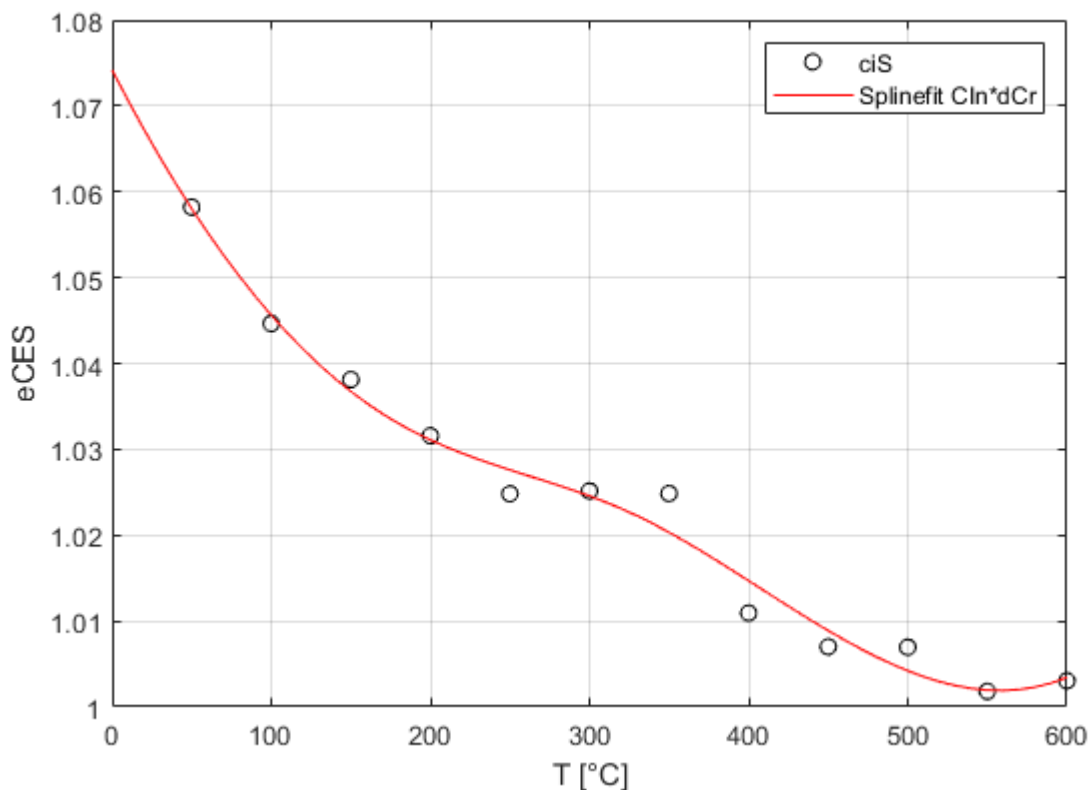
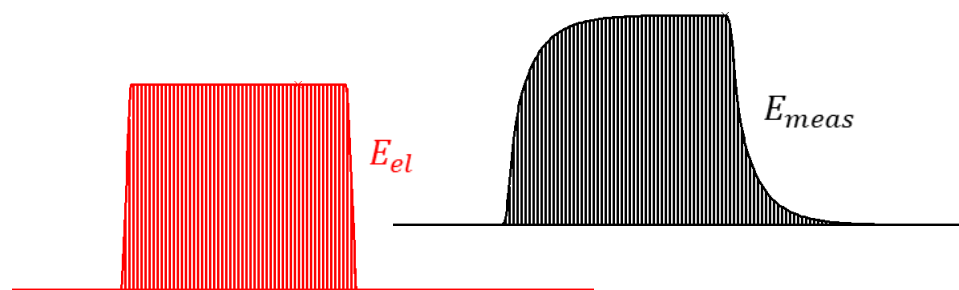


- Pulse areas are integrated and the ratio

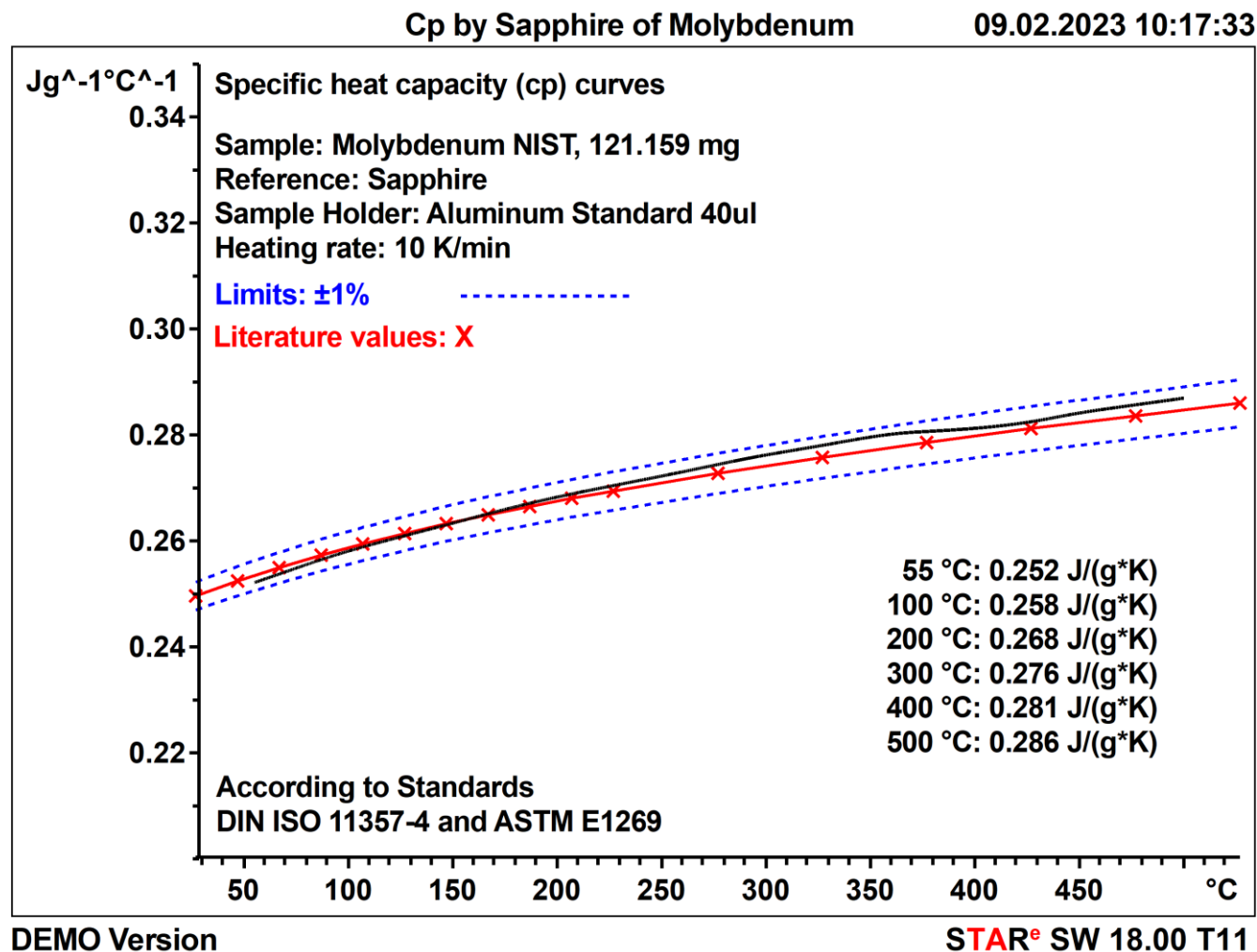
$$C = \frac{E_{meas}}{E_{el}}$$

is obtained for each pulse.

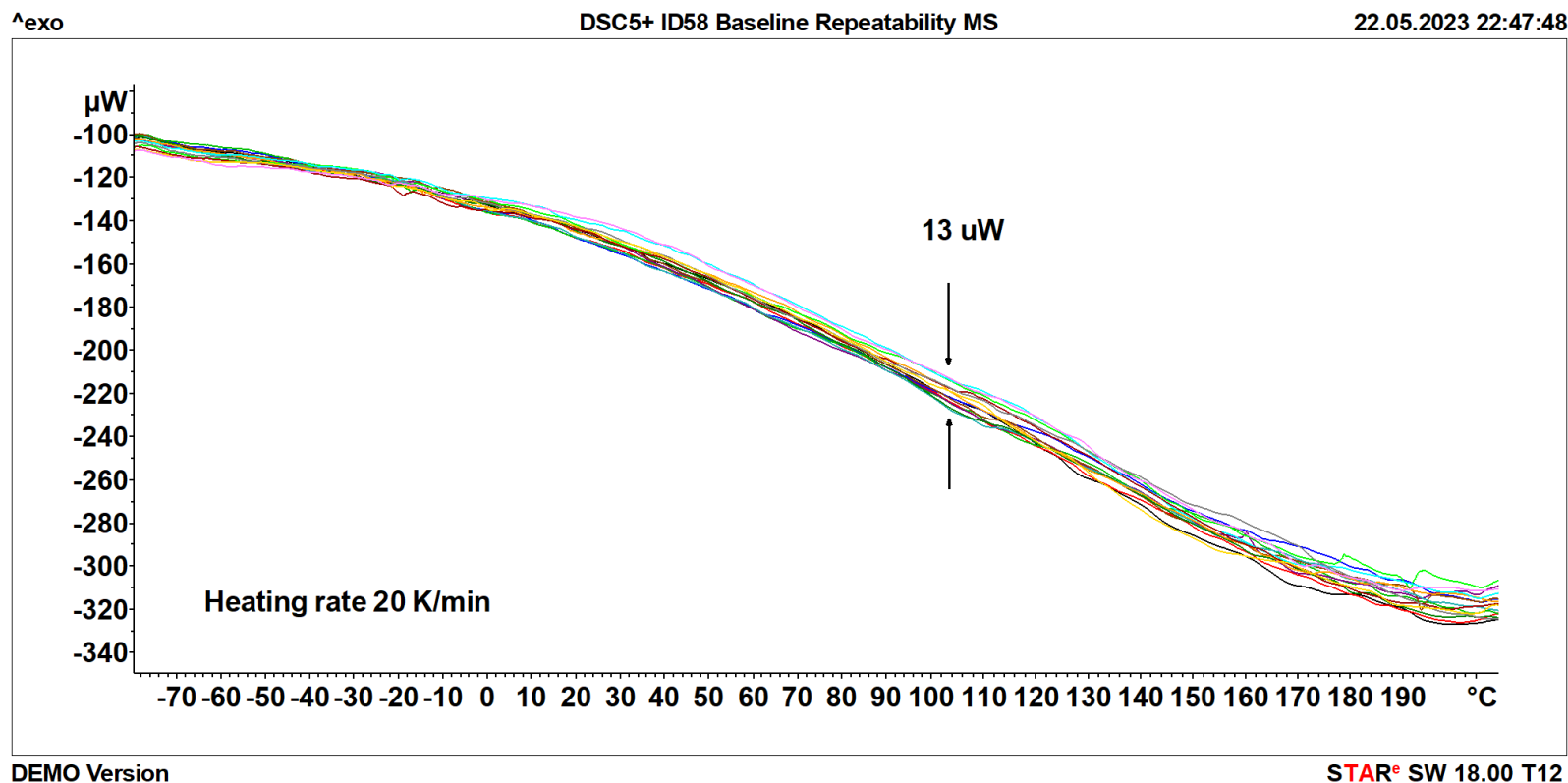
- A curve is fitted through the points and saved (electrical adjustment curve).
- The sensitivity curve is calculated and saved.

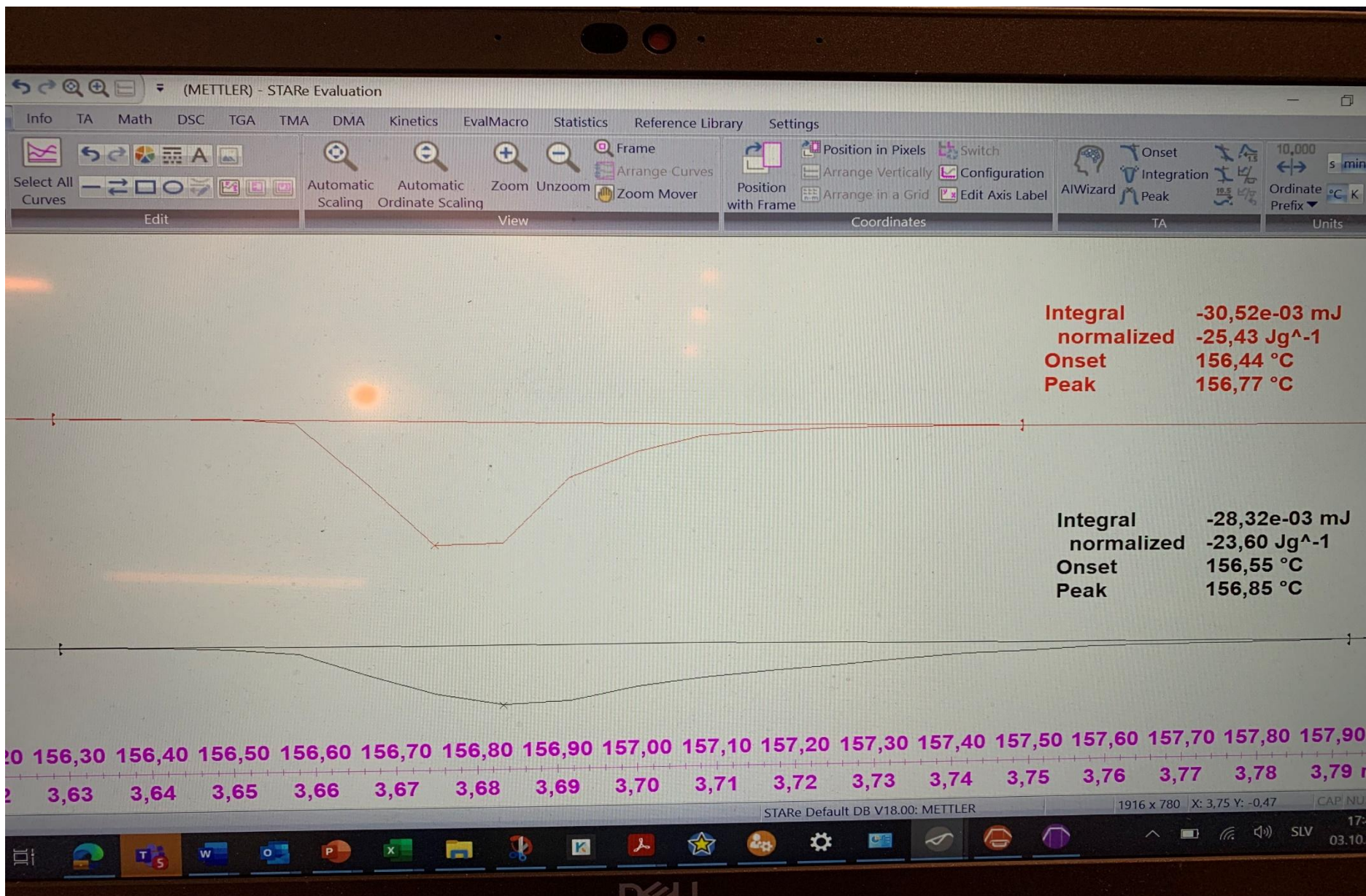


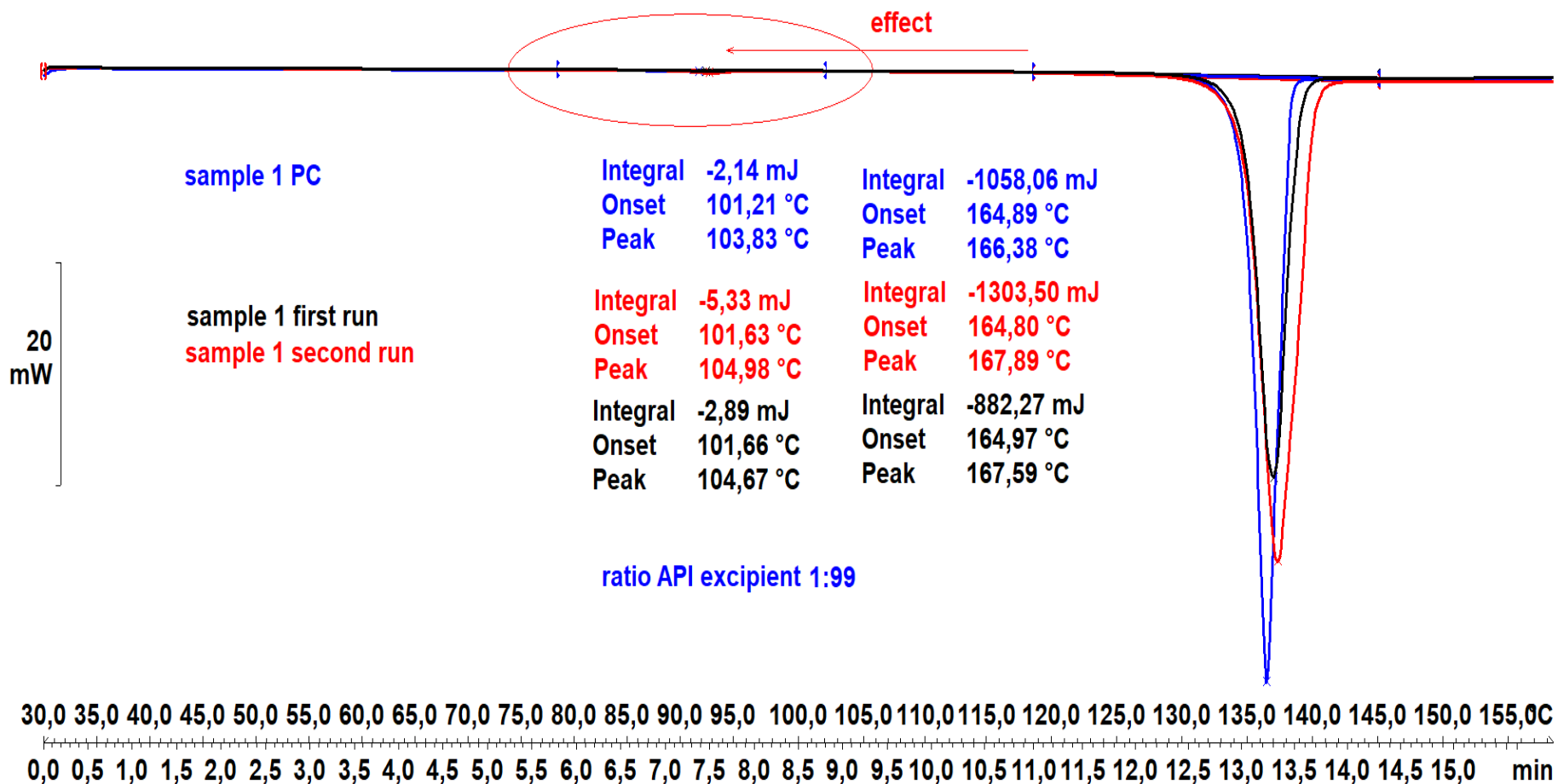
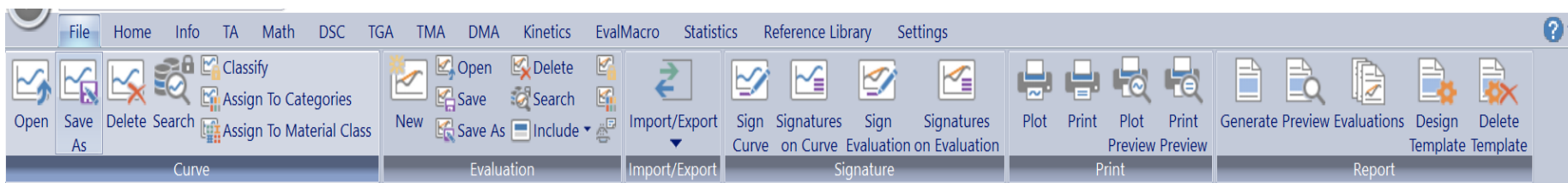
Real measurements show an accuracy of better than 1% (DSC 3+: ~5%).

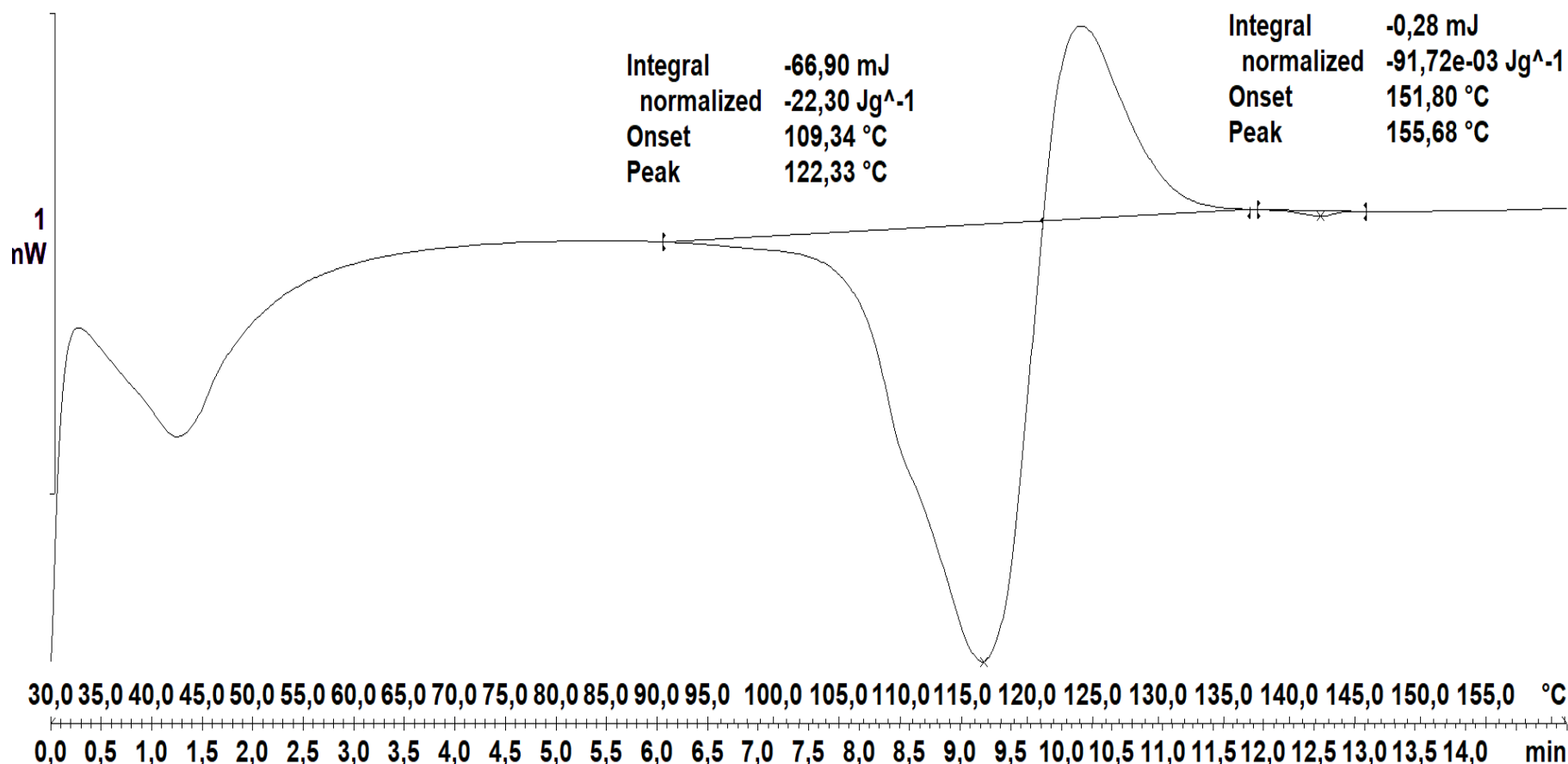
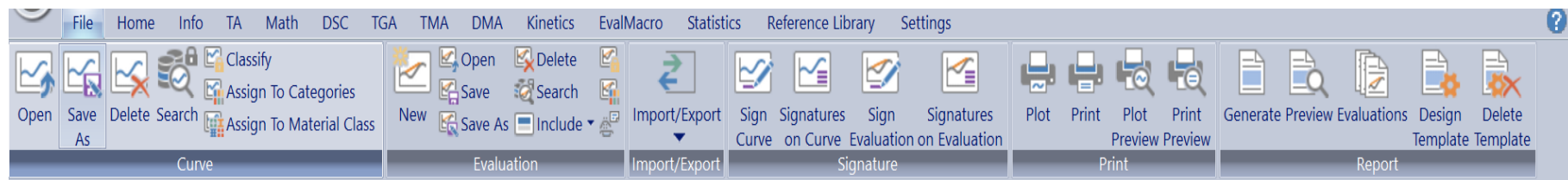


- Excellent baseline repeatability
- Intracooler / LN2 combi cooler
- Exchangable reference crucible
- Exchangable reference crucible
- 4 gases
- Power compensation or heat flux mode
- Electric HF adjustment, calibration with CRM's









Jürgen E.K. Schawe
Mettler-Toledo GmbH



Metastable Phases in Bulk Metal glasses BMG Alloys

METTLER TOLEDO



Jürgen E.K. Schawe ✓

Dr. rer. nat. - Senior Researcher at ETH Zurich

Contact

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134

Publications

26,405

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4,039

Citations

Introduction

Main interest: The investigation of transformations in metastable materials such as polymers and metal alloys using thermal analysis techniques. This includes the kinetics of glass transition, crystallization and melting kinetics as well as solid-solid transformations and diffusion-controlled chemical reactions. Main techniques: DSC, Temperature Modulated DSC, Fast DSC (Flash DSC), DMA and solid-state rheometry. Development of measurement, evaluation and sample preparation methods.

Current institution

ETH Zurich

Metal Physics and Technology Gr...



Current position

Senior Researcher

**Laboratory of Metal Physics and Technology,
Prof. J.F. Löffler**

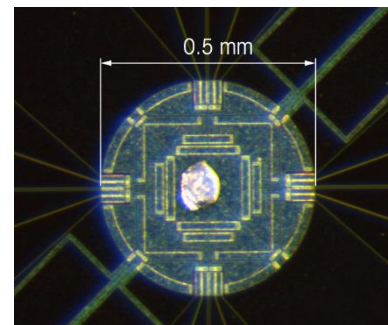
Co-authors

METTLER TOLEDO



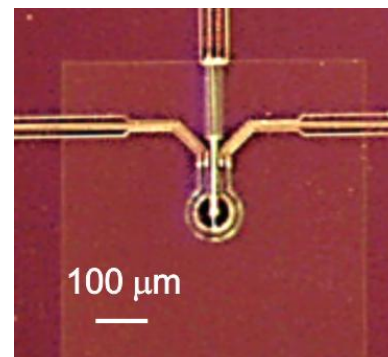
Sensor UFS1: -95 °C .. 520 °C

- 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



X. Ueber physikalische Isomerie.

Von

O. Lehmann in Freiburg i. B.*)

(Hierzu Tafel V.)

Einleitung.

Mit dem Namen »physikalische Isomerie« bezeichnet die neuere Chemie das Auftreten derselben chemischen Verbindung in mehreren, durch ihre physikalischen Eigenschaften unterschiedenen Modifikationen, deren Existenz sich nicht durch verschiedene Anordnung der Atome im Molekül erklären lässt, und welche ausserdem charakterisirt sind durch die Leichtigkeit, mit welcher sie sich durch rein physikalische Mittel (Wärme) in einander umwandeln lassen.

Physical polymer (Enantiotropy):

Transition of a stable modification in a stable modification

Physical metamere (Monotropy):

Possible coexistence of a metastable and a stable modification



ZEITSCHRIFT

FÜR

KRYSTALLOGRAPHIE

UND

MINERALOGIE

UNTER MITWIRKUNG

ZAHGREICHER FACHGENOSSEN DES IN- UND AUSLANDES

HERAUSGEGEBEN

VON

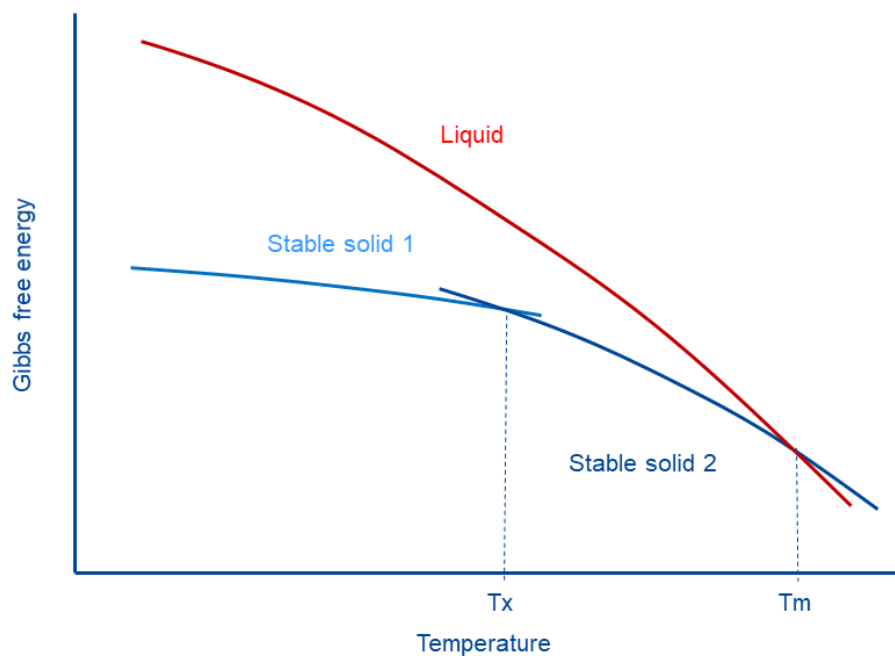
P. GROTH.

LEIPZIG,

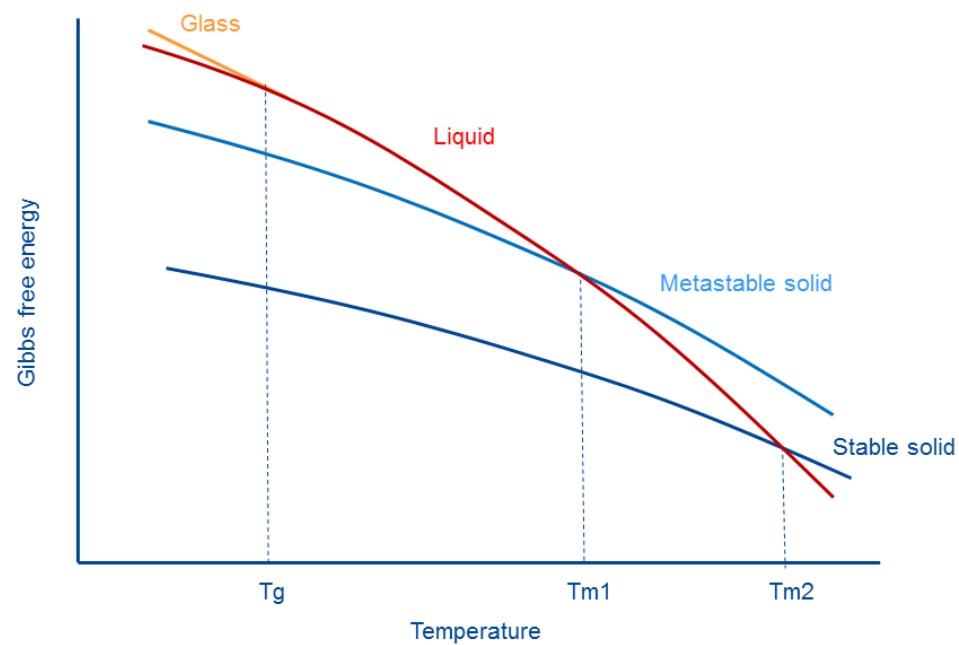
VERLAG VON WILHELM ENGELMANN.

1877.

Enantiotropy



Monotropy





Studien über die Bildung und Umwandlung fester Körper.

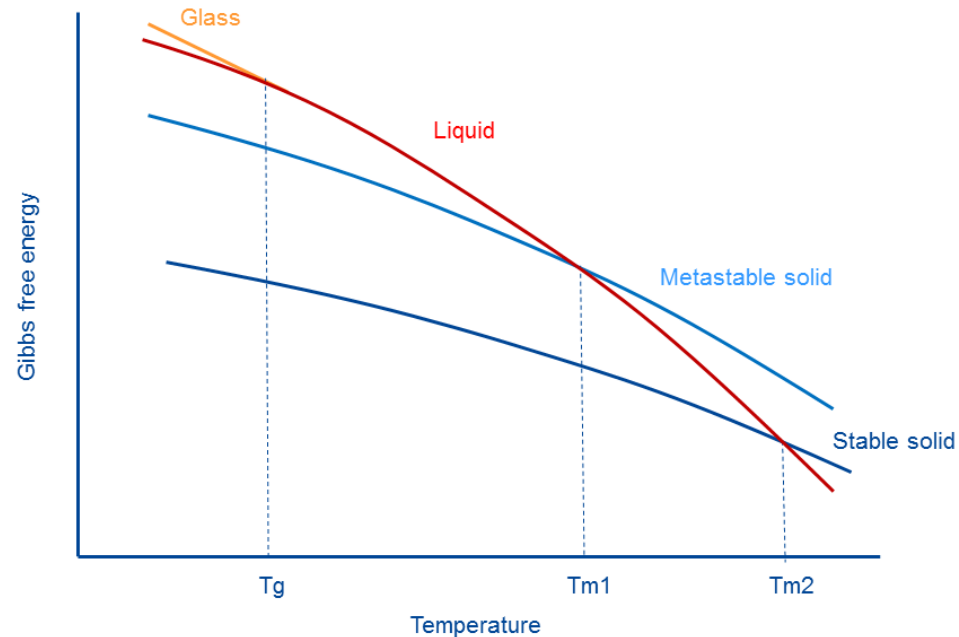
1. Abhandlung: Übersättigung und Überkaltung.

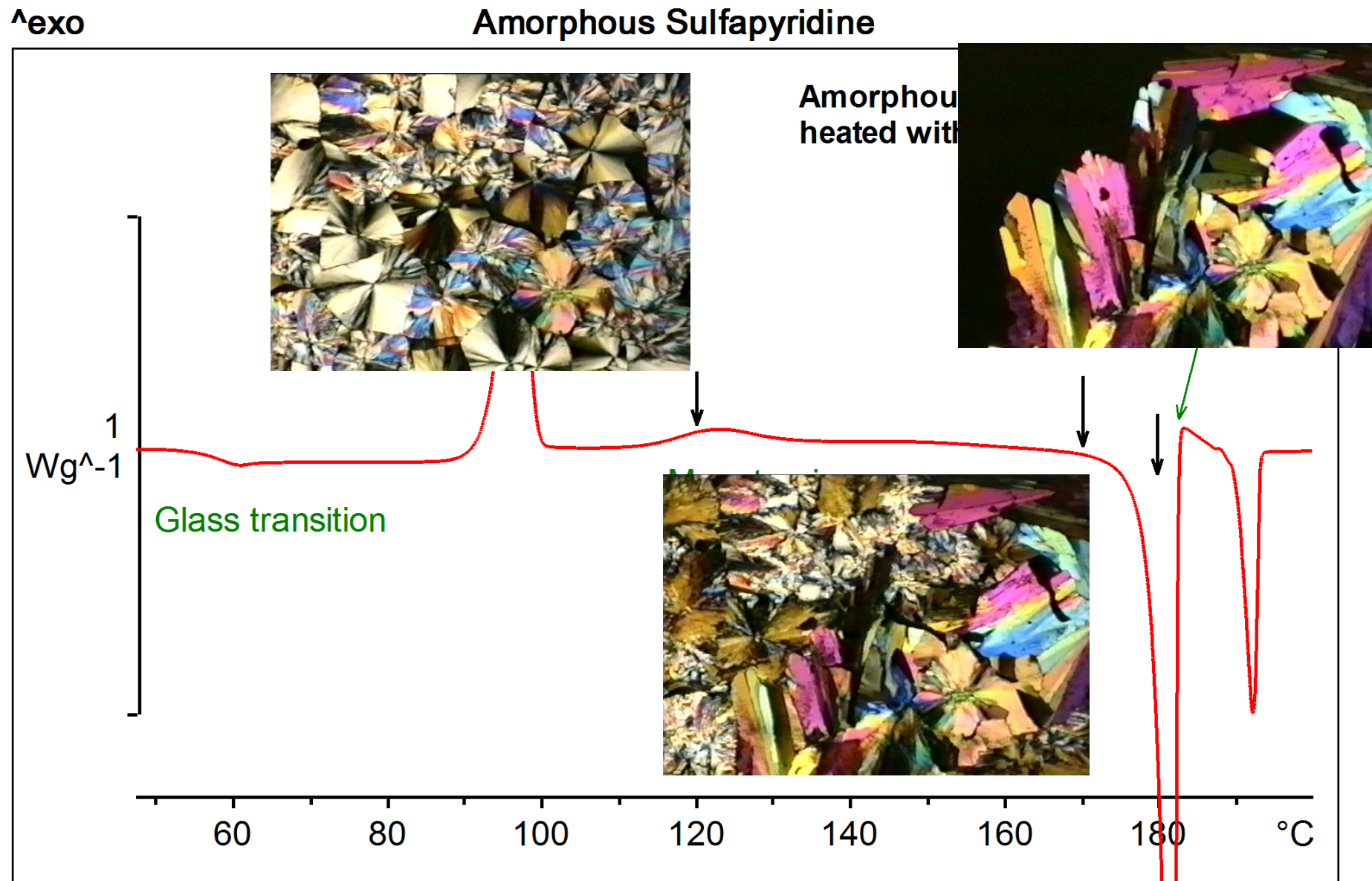
Von
W. Ostwald.

(Mit 6 Figuren im Text.)

In Veranlassung der Abfassung einiger Kapitel meines Lehrbuches der allgemeinen Chemie habe ich mehrere bereits bekannte Versuche bezüglich der Bildung fester Körper aus Lösungen und Schmelzen, sowie ihrer polymorphen Umwandlungen wiederholt, um die Erscheinungen aus eigener Anschauung kennen zu lernen. Dabei ergab sich alsbald eine Anzahl von Fragen und Problemen, deren Verfolgung mich in eine ziemlich verzweigte experimentelle Untersuchung führte. Von den Ergebnissen dieser Arbeiten, die ich aus naheliegenden Gründen nur lang-

Monotropy





- 1** Introduction
- 2** Metallic Glass
- 3** Phases in Metallic Glass Forming Alloys
- 4** Differently Nucleated Glass
- 5** Stability of Glasses
- 6** Additive Manufacturing
- 7** Summary



1903

KRISTALLISIEREN UND SCHMELZEN

EIN BEITRAG ZUR LEHRE DER ÄNDERUNGEN DES
AGGREGATZUSTANDES

VON

GUSTAV TAMMANN

O. Ö. PROFESSOR AN DER UNIVERSITÄT ZU GÖTTINGEN

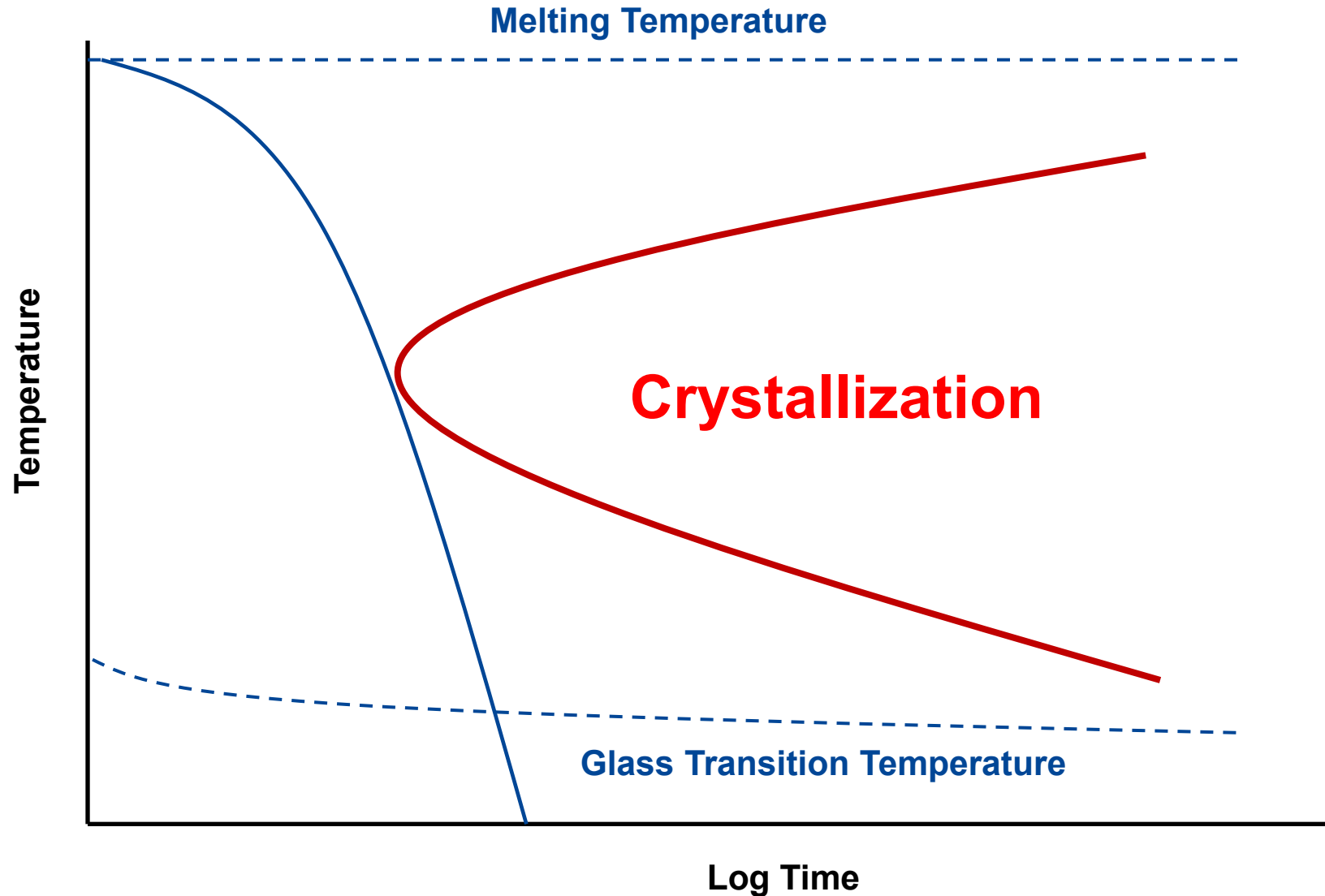
MIT 88 ABBILDUNGEN

Die Untersuchung des spontanen Kristallisationsvermögens hat zum Resultat geführt, daß dasselbe zuerst mit der Entfernung vom Schmelzpunkt zunimmt, dann aber von einer gewissen Temperatur an, die für jeden Stoff charakteristisch ist und sich durch Zusätze wenig ändert, abnimmt. Kühlt man also einen Stoff so ab, daß seine Temperatur möglichst schnell das Temperaturintervall, in dem sich eine größere Anzahl von Kristallisationszentren in der Zeiteinheit bildet, durchschreitet, so muß man denselben, da die innere Reibung mit abnehmender Temperatur schnell wächst, im Zustande eines Glases oder amorphen festen Stoffes erhalten. Es müßte also möglich sein, *alle Stoffe in Form von Gläsern zu realisieren*, während man früher annahm, daß in diesen Zustand nur Gemenge übergeführt werden könnten. Um dieser Frage näher zu treten, wurde eine statistische Untersuchung an 153 Stoffen vorgenommen. Jeder derselben wurde in eine

The glass formation dependence on nucleation and crystal growth.

The cooling rate is the important property to form a glass.

At sufficient fast cooling all or the most materials can form a (partial) glass.



No. 4740 September 3, 1960

NATURE

869

METALLURGY

Non-crystalline Structure in Solidified Gold-Silicon Alloys

EXCEPT for thin films deposited at very low temperatures¹, highly disordered arrangements of the atoms, similar to that of the liquid state, have never been observed in solid metals and alloys. For some metalloids, the bonding of which may actually be more covalent than metallic, such amorphous configurations have been retained in the solid state² by cooling from the melt with sufficient celerity so as to prevent formation of the equilibrium crystalline structures.

It is thus conceivable that such non-crystalline structures can be obtained for some, perhaps all, metals and alloys by quenching rapidly enough from the molten state. In the course of experimentation with the apparatus developed by us³, an amorphous structure has been detected in a 25 atomic per cent silicon-gold alloy which was quenched from $\sim 1,300^\circ$ C. to room temperature.

The quenched alloy was studied by means of X-ray diffraction. A flake (area ~ 0.2 mm.²; thickness $\sim 10\mu$) was mounted in a Debye-Scherrer camera and exposed to copper *K* radiation. Intensity (on an approximately linear scale), as obtained from the film with a microphotometer, is plotted against $\sin \theta/\lambda$ in Fig. 1.

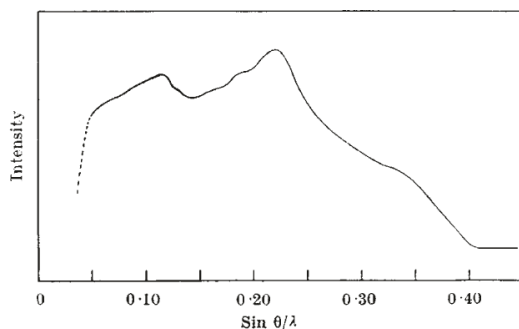


Fig. 1. X-ray diffraction pattern of gold-silicon alloy

It is to be emphasized that the amorphous foil is quite unstable at room temperature (and it is entirely possible that some decomposition could have occurred during the 3-hr. exposure). The decomposition products detected after 24 hr. at room temperature have complex crystal structures, involving *d*-spacings of the order of 11–12 Å. It is quite probable that many phases may be present under these non-equilibrium conditions. However, at this stage of decomposition, the equilibrium phases are definitely not present.

Since the synthesis and investigation of these amorphous foils are highly uncertain under the present experimental conditions, refinement of the apparatus so as to permit operation at liquid-nitrogen temperatures is now under way. Among the various facets of such non-crystalline metals and alloys which might be of interest, possible superconducting properties should be considered—especially since Buckel¹ has observed that certain metals in thin evaporated layers (amorphous structure) become superconducting at somewhat higher temperatures than with the normal crystal structures.

This work was jointly supported by the Office of Naval Research and the U.S. Atomic Energy Commission.

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

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

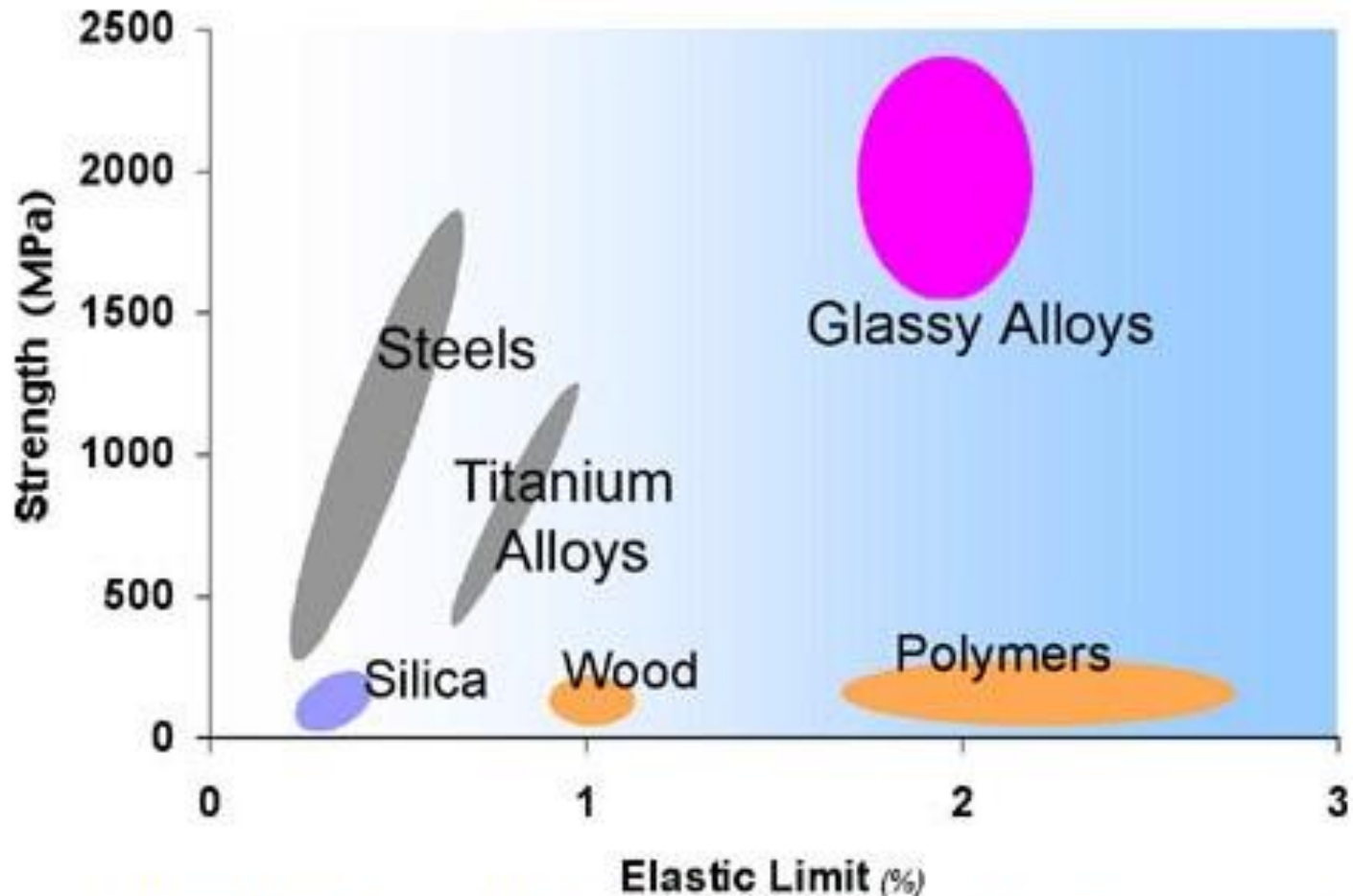
¹ Buckel, W., *Z. Physik*, **138**, 136 (1954).

² Krebs, H., and Schultze-Gebhardt, F., *Acta Cryst.*, **8**, 412 (1955).

³ Pol Duwez, Willen, R. H., and Klement, jun., W., *J. App. Phys.* **31**, 1136 (1960).

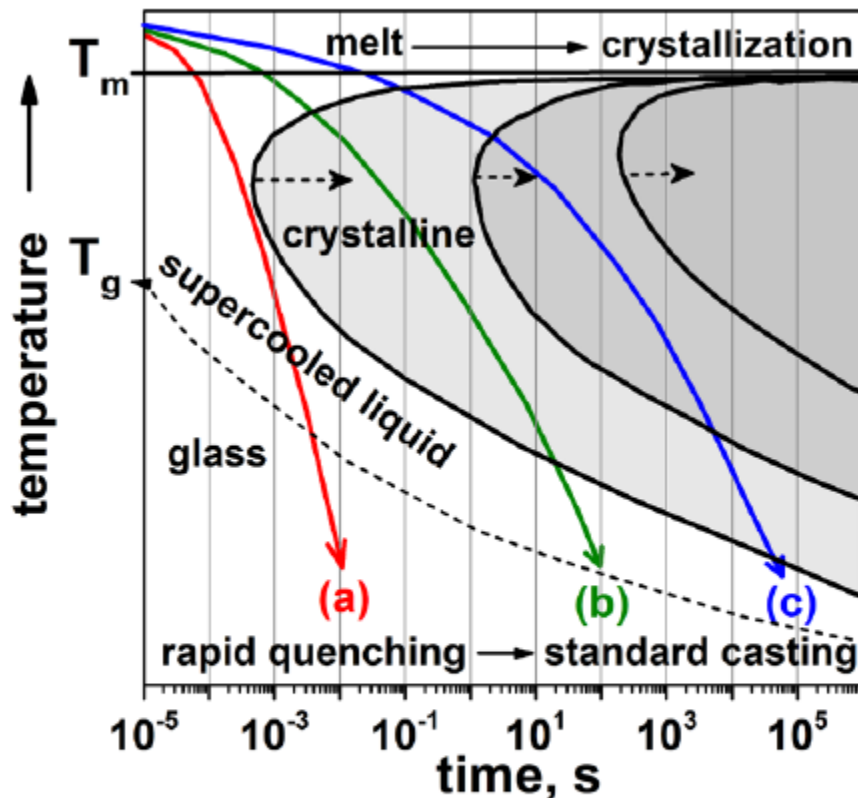


Pol Duwez



Typical strengths and elastic limits for various materials. Metallic glasses are unique.

Bulk metallic glasses (BMG) vs. conventional metallic glasses

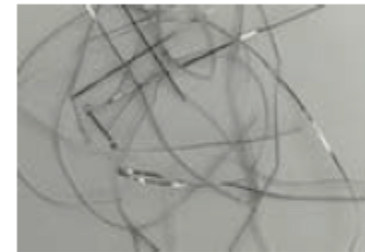


See, e.g., W.L. Johnson, Bull. Mater. Sci. Society, Oct. 1999;
R. Busch, I. Gallino, JOM-J Min. Met. Mat. S. 69 (2017) 2178

a) Conventional metallic glass with
critical cooling rates of 10^5 - 10^6 K/s

since 1959

RAPID QUENCH



b) Metallic glasses with
critical cooling rates of 100 K/s
since 1974

c) Bulk metallic glass (BMG)
with critical cooling rates of ~ 1 K/s

since early 1990s

STANDARD
CASTING



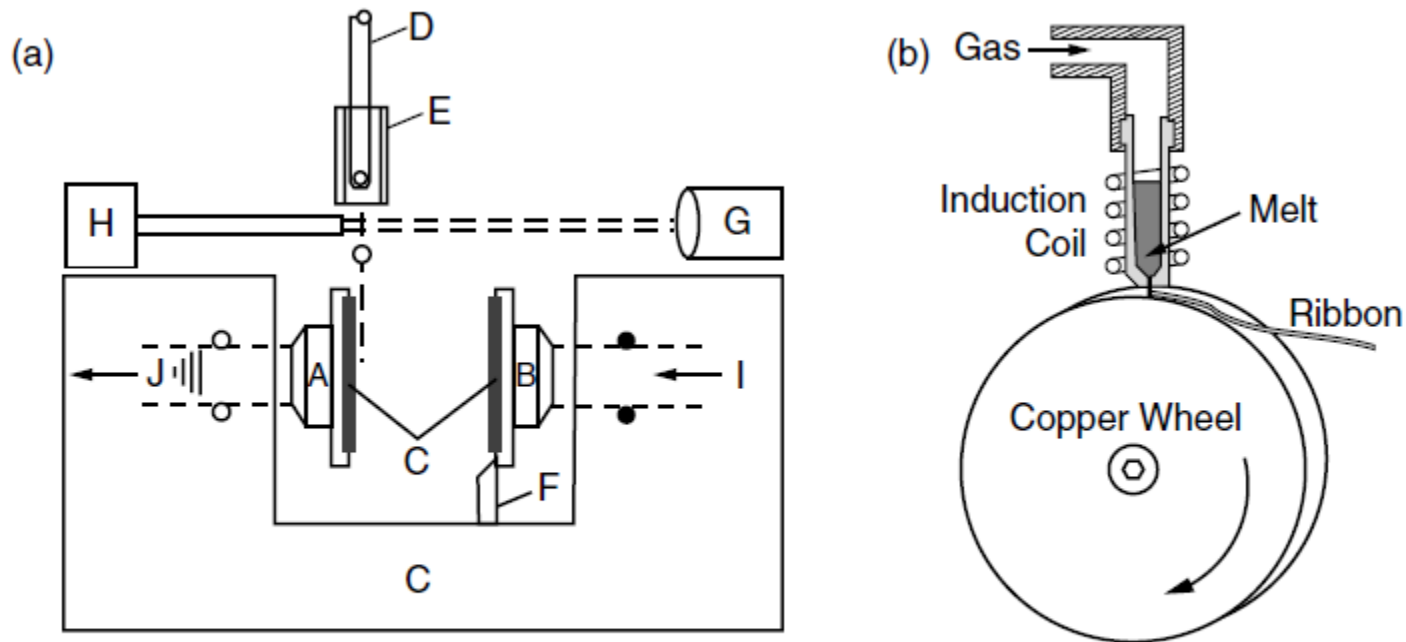


FIGURE 17.4 Schematic drawing of (a) splat quencher and (b) melt spinner. (17.4a from Johnson, W.L., *Metals Handbook* 2, 805, 1990. With permission.)

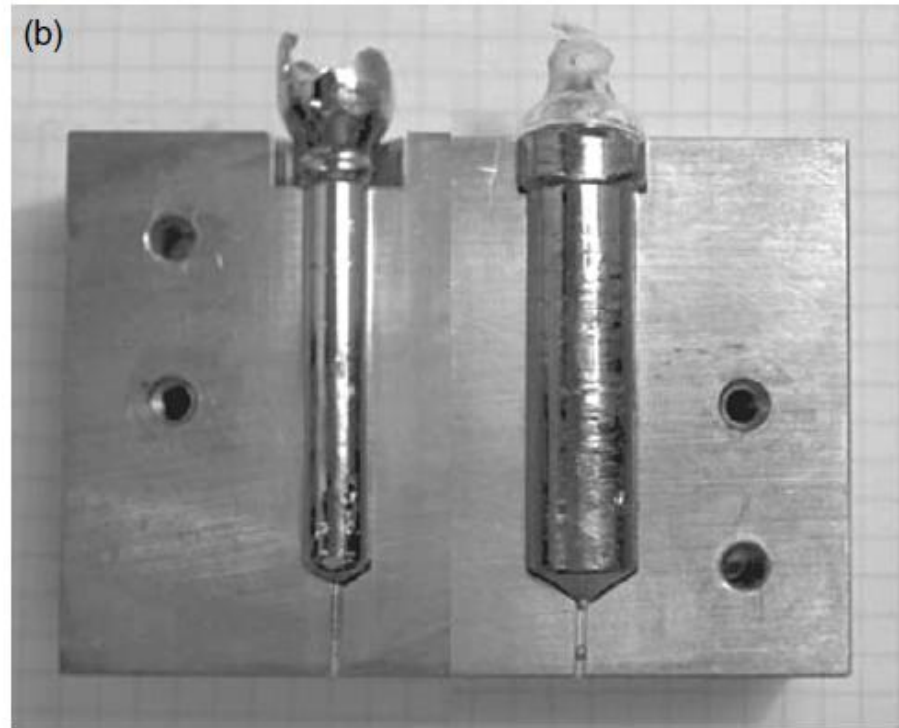
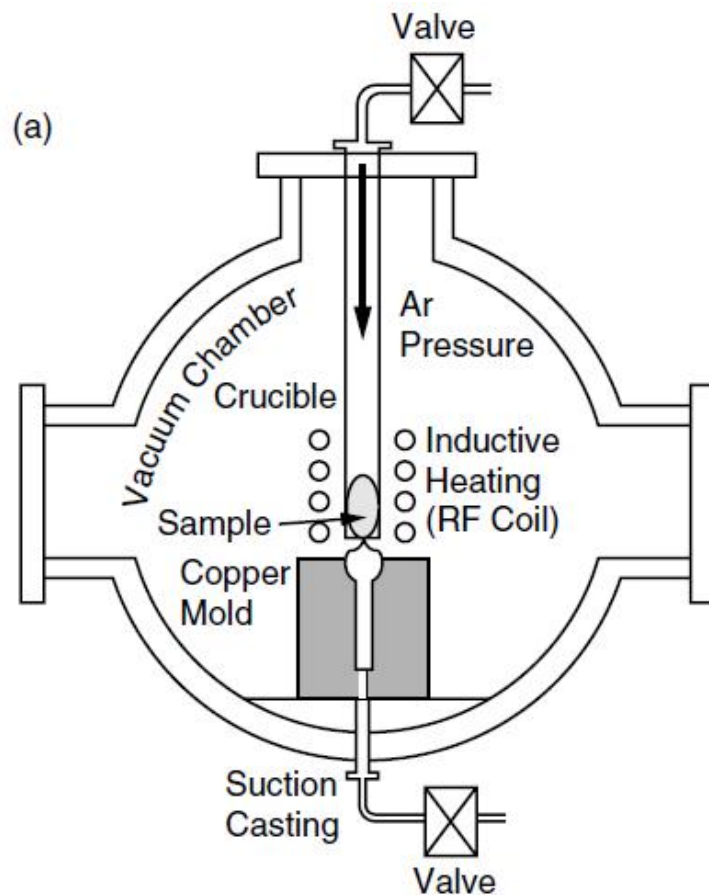
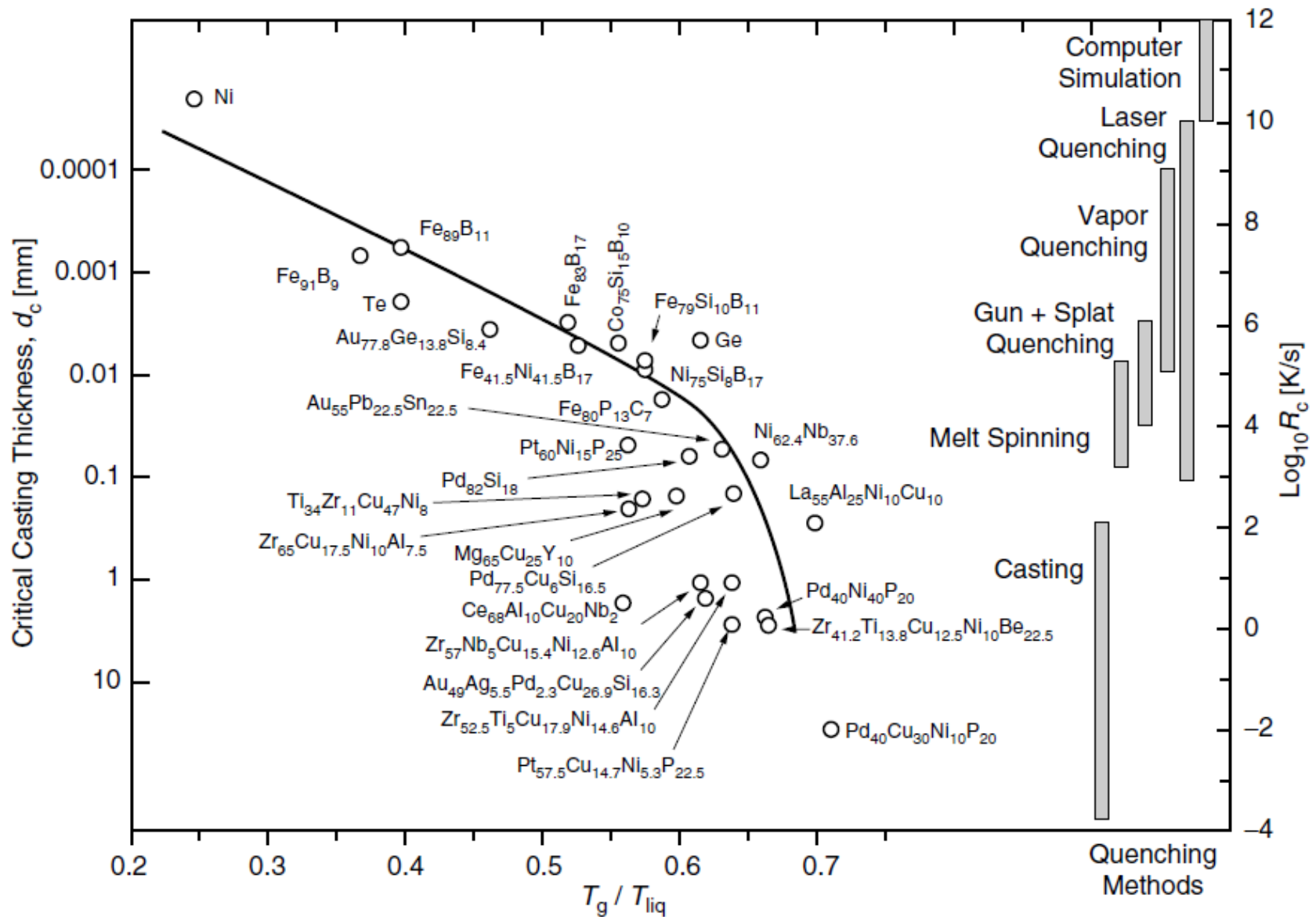


FIGURE 17.5 (a) Schematic drawing of a casting box, in which the samples are inductively heated and cast by either suction or pressure injection; (b) close-up photograph of a copper mold with cast Zr-based bulk metallic glass samples of diameters 5 and 10 mm.



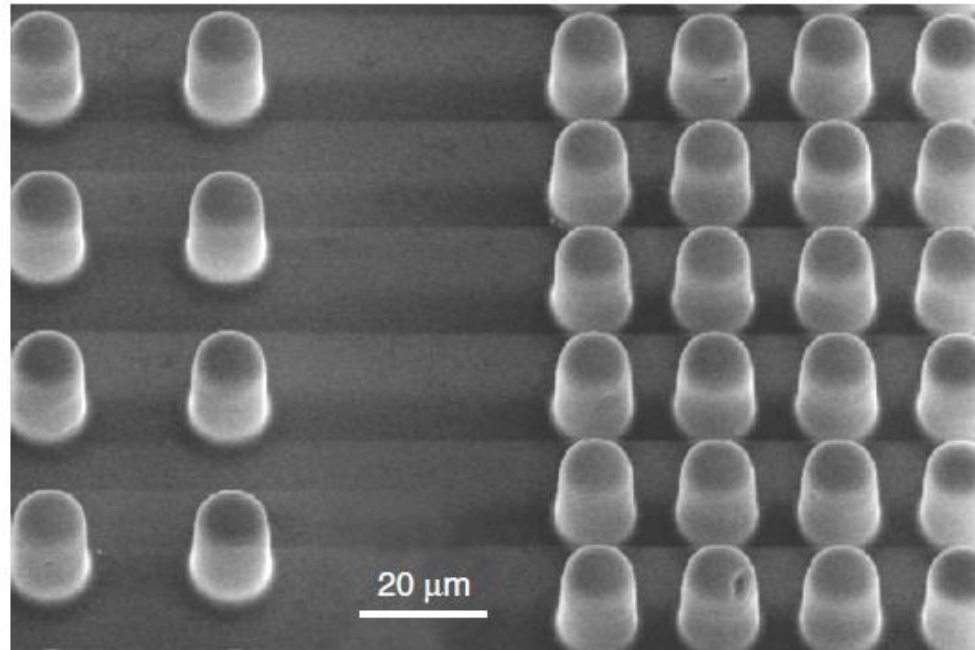


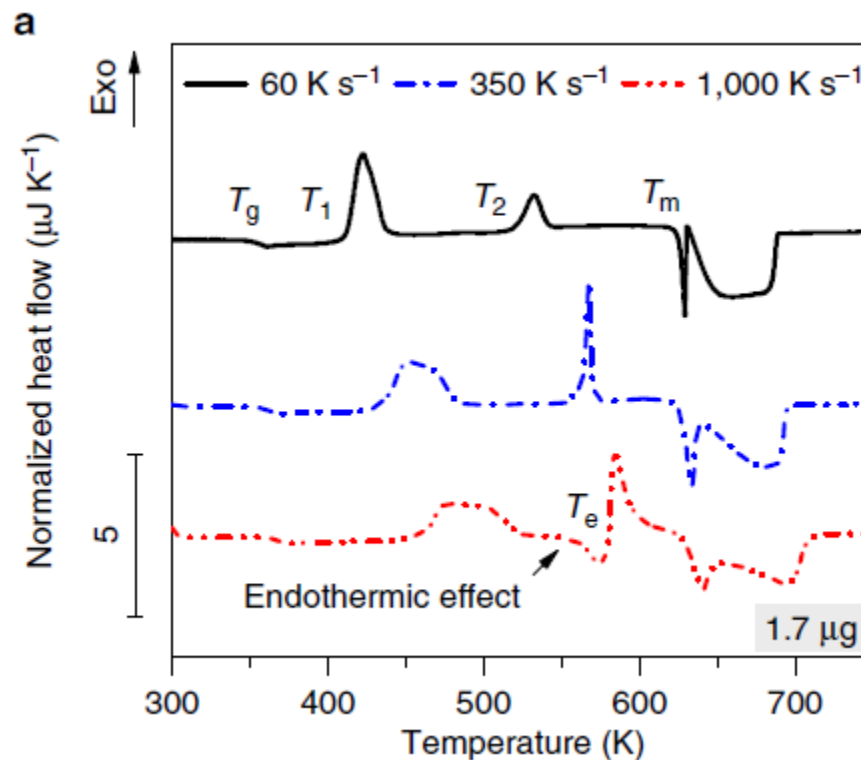
FIGURE 17.17 Pins of 20 μm in height and 8 μm in diameter of a bulk metallic glass, replicated from a surface-microstructured Si wafer by rapid cooling from the melt.

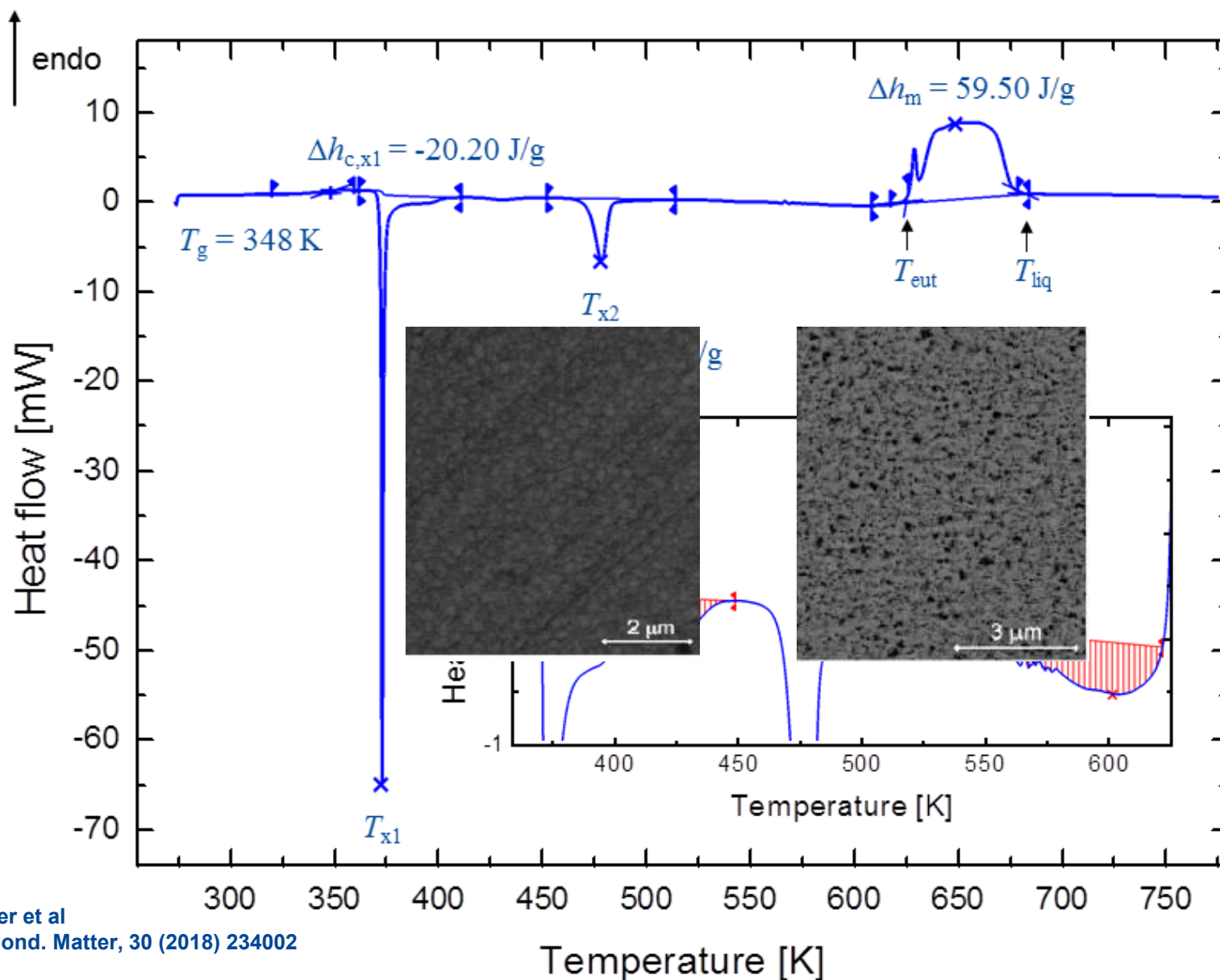
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Solid-solid phase transitions via melting in metals

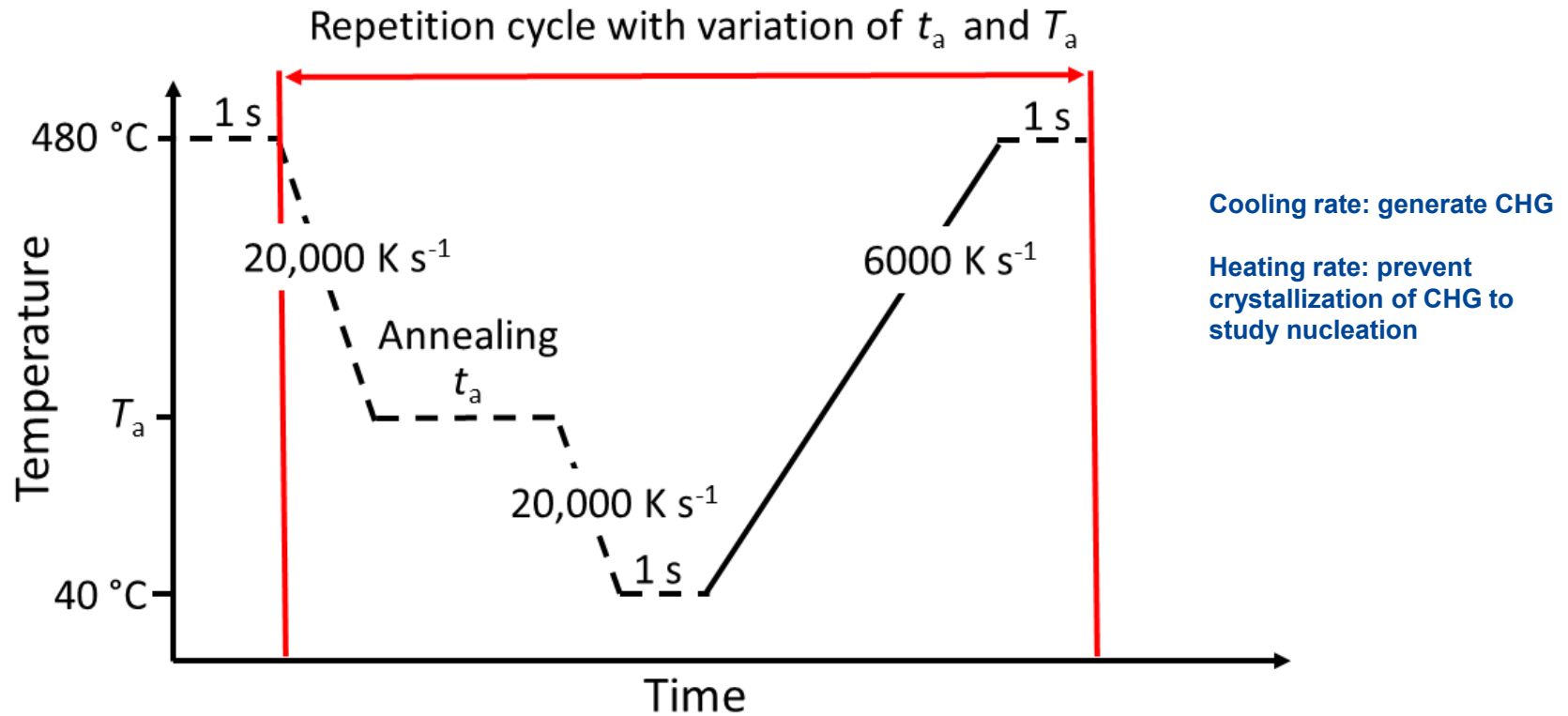
S. Pogatscher^{1,2}, D. Leutenegger¹, J.E.K. Schawe³, P.J. Uggowitzer¹ & J.F. Löffler¹

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

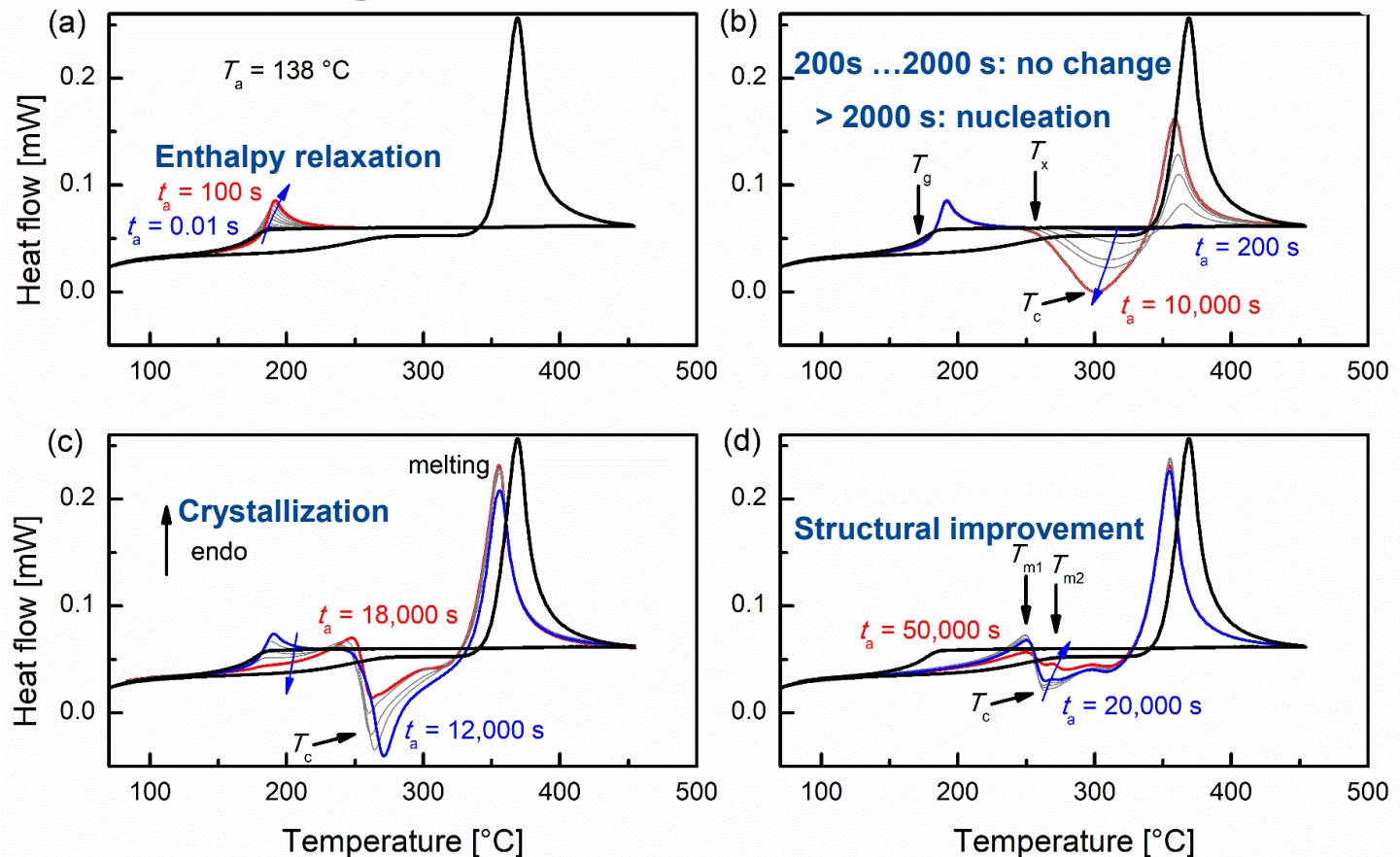
 $\text{Au}_{70}\text{Cu}_{5.5}\text{Ag}_{7.5}\text{Si}_{17}$ BMG

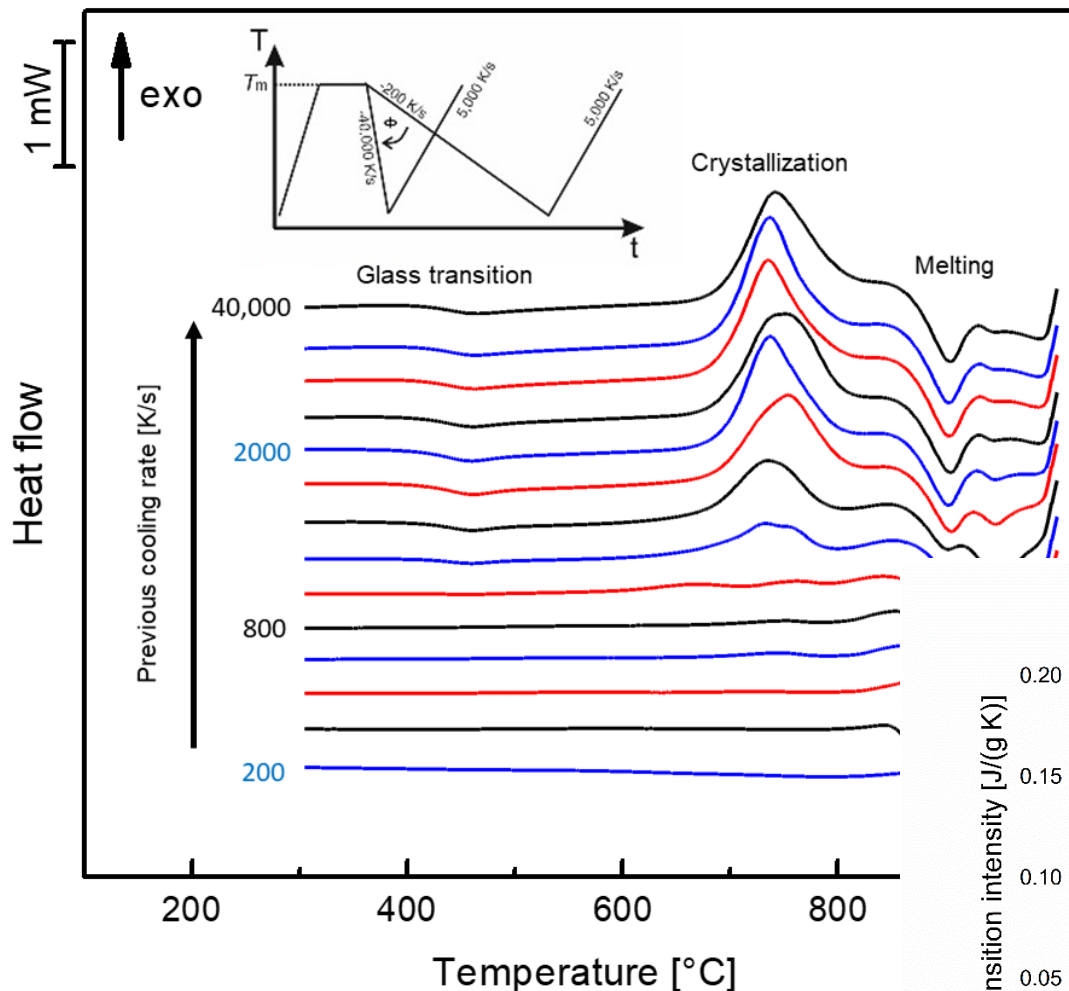


Temperature program

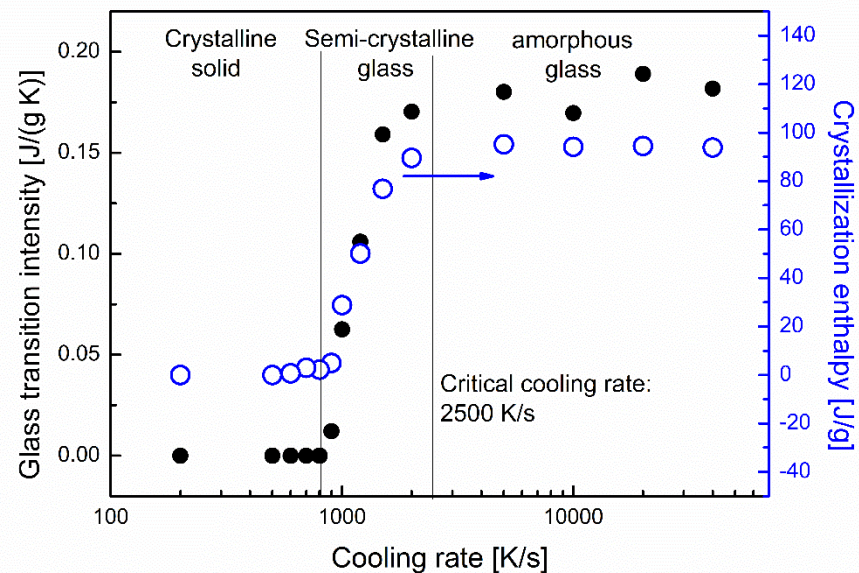


Annealing at 138 °C of CHG



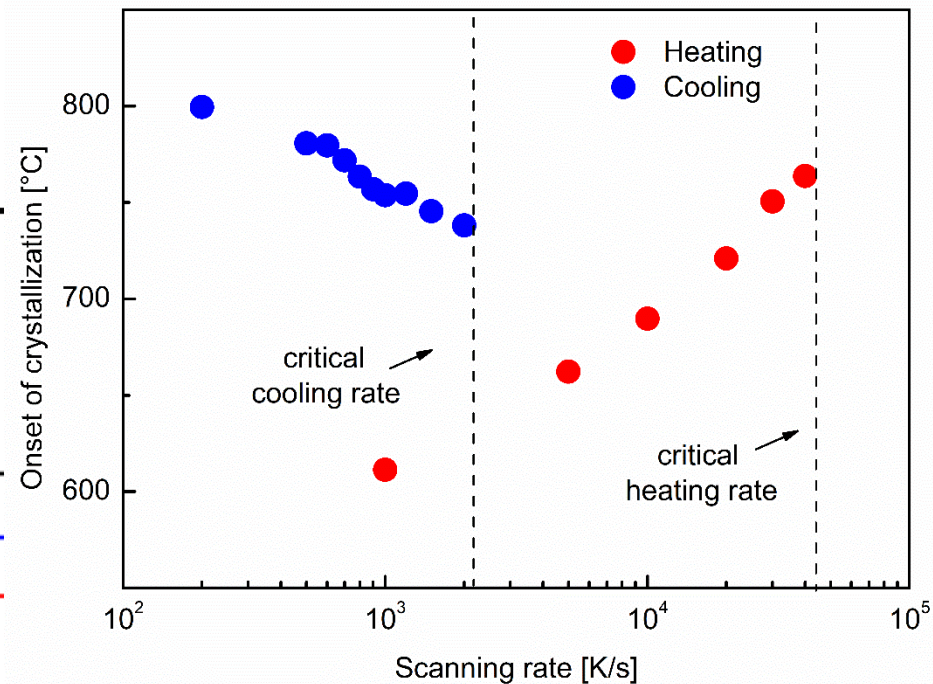
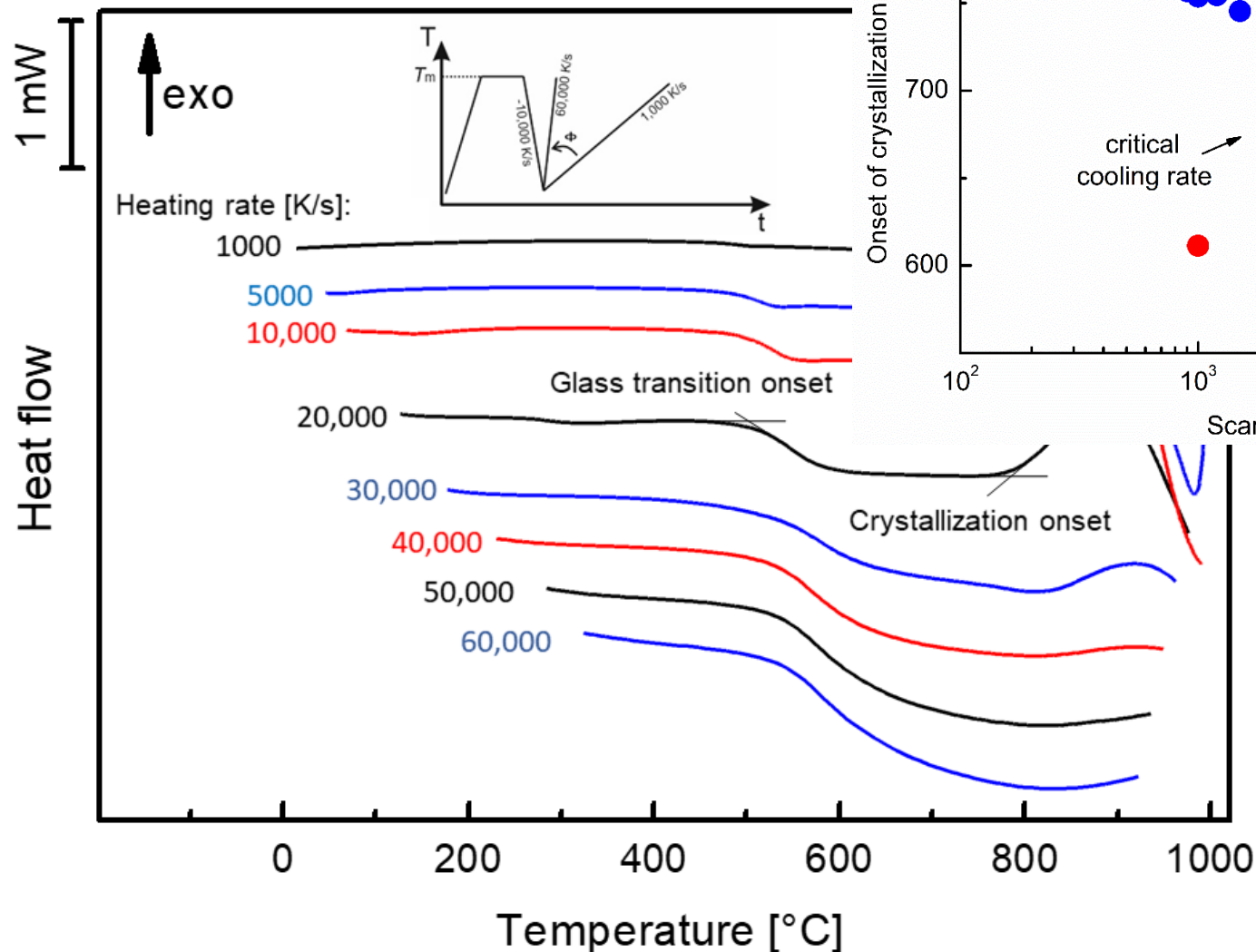


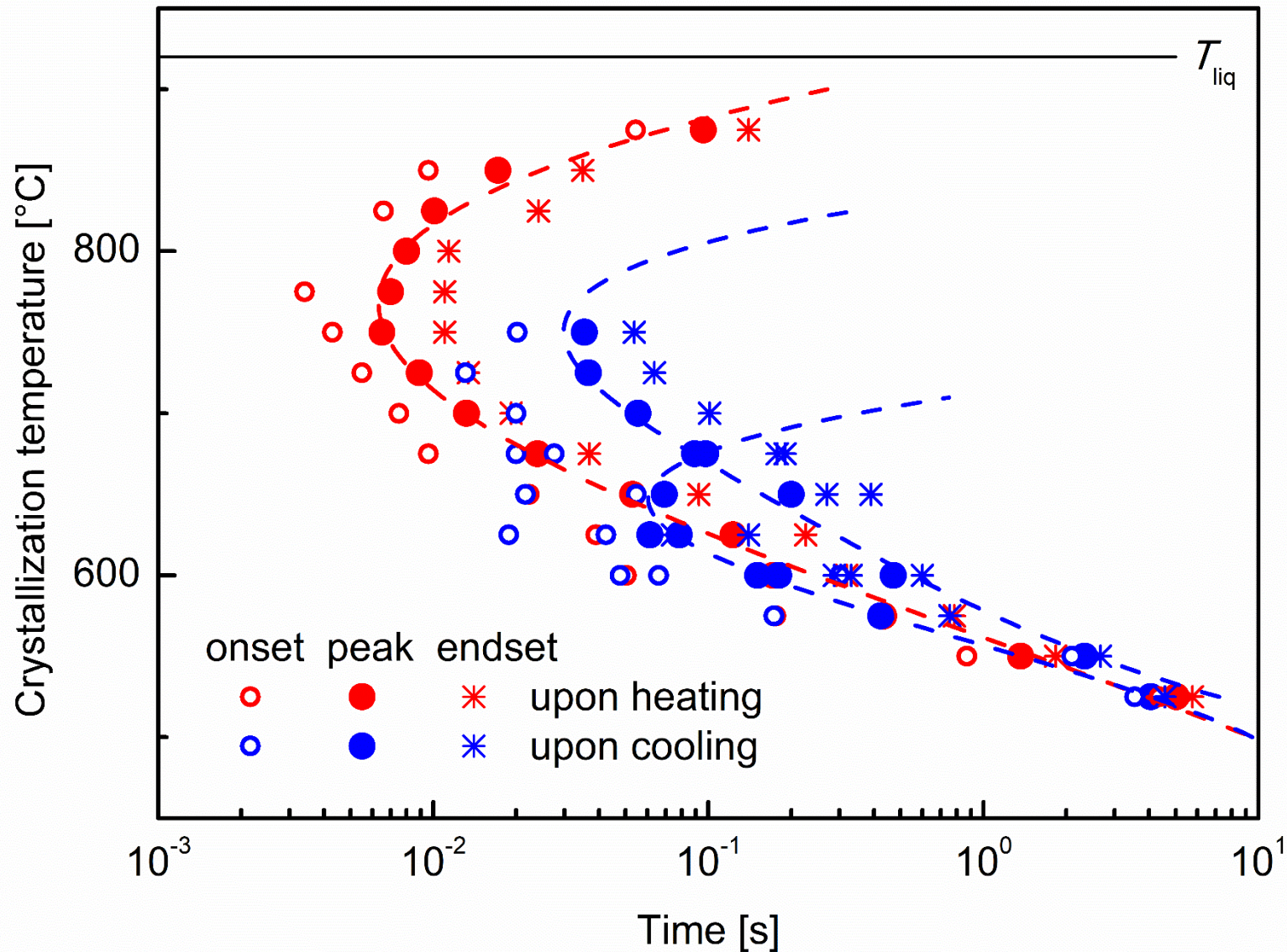
N. Sohrabi, J.E.K. Schawe, J. Jhabvala, J.F. Löffler, R.E. Logé
 Critical crystallization properties of an industrial-grade Zr-based metallic glass
 Scripta Materialia, 199 (2021) 113861



Heating of $\text{Zr}_{59.3}\text{Cu}_{28.8}\text{Al}_{10.4}\text{Nb}_{1.5}$

N. Sohrabi, J.E.K. Schawe, J. Jhabvala, J.F. Löffler, R.E. Logé
Critical crystallization properties of an industrial-grade Zr-based metallic
glass
Scripta Materialia, 199 (2021) 113861





Thank you

Hvala

Köszönöm

Vielen Dank

