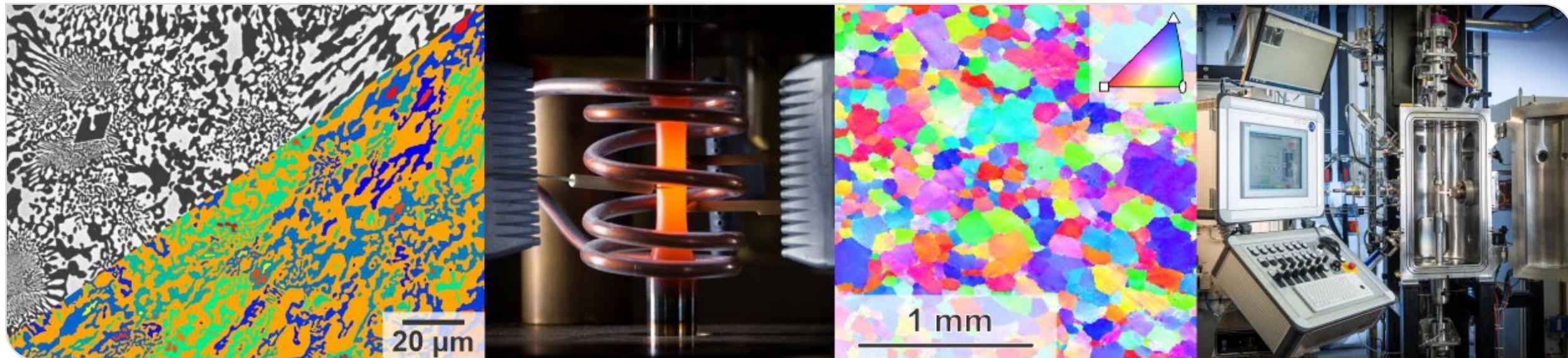


Phase Transformations in Materials

Lecture for “Mechanical Engineering” and “Materials Science and Engineering”
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Topics

- Experimental techniques
 - General Terms
 - Structural Investigations
 - Physical Investigations
 - Chemical Investigations
 - Microstructural Investigations

General Terms

- In general, phase transformations are investigated:
 - **Ex situ**: The phase transformation occurs either completely or partially under specific conditions and the examination of the result is investigated **subsequent** to this.
 - **In situ**: The phase transformation occurs **while** the investigation is running so that the conditions during investigation and phase transformation are essentially the same.

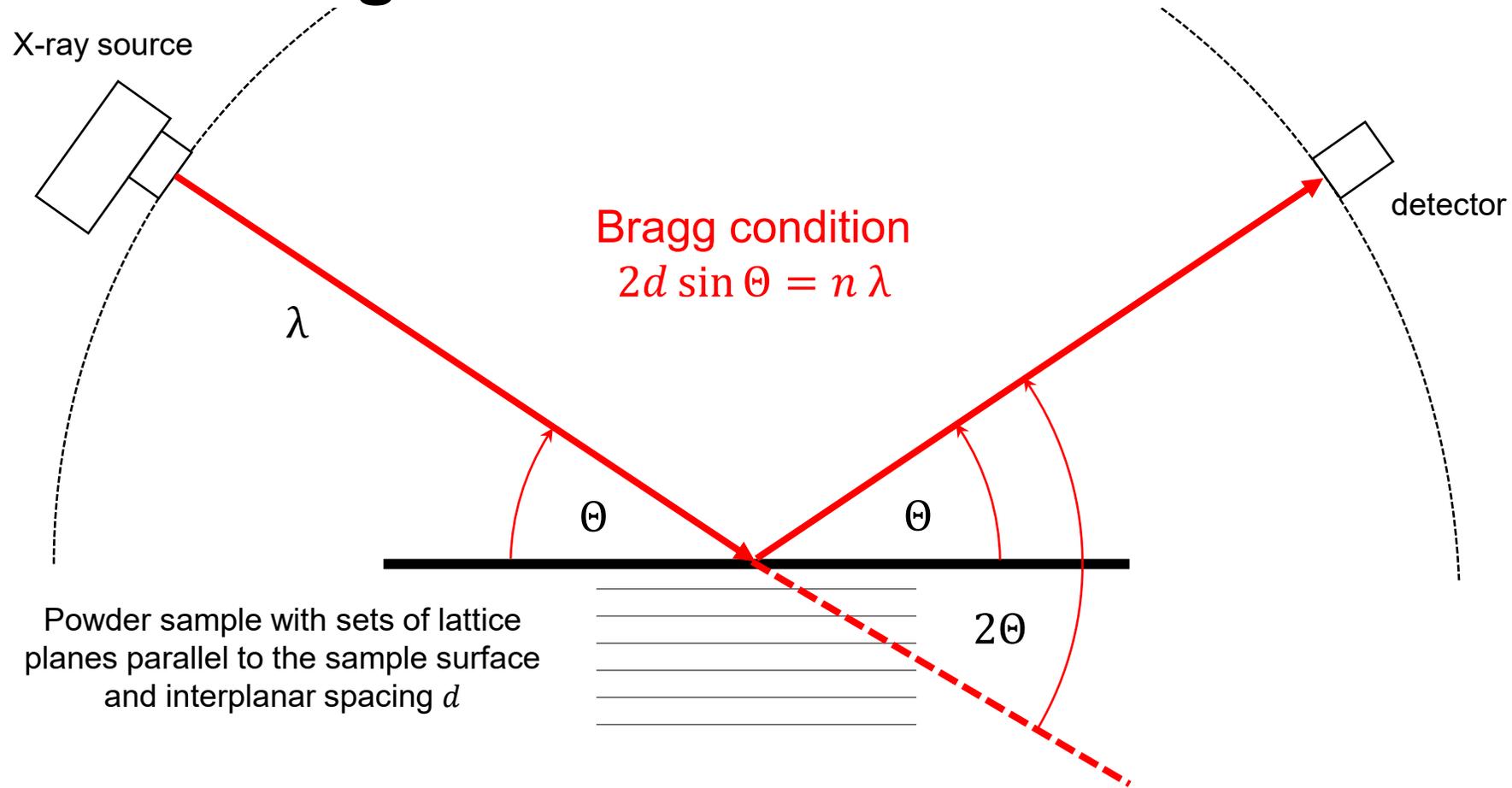
General Terms

- For materials science related problems following specific issues are typically investigated during or subsequent to phase transformations:
 - **Structural information**, mainly crystallographic, by **diffraction** of **X-rays** (lab-based, synchrotron), **electrons** (in most cases lab-based), or **neutrons** (large scale research facilities); in rare cases, also other beams might be utilized, like muons, heavy ions, etc.
 - **Physical information**, like **specific heat**, **latent heat**, **strain**, **density**, **electrical resistivity**, **electric polarization**, **magnetization**, etc.
 - **Chemical information**, e.g. **composition of phases**/regions in materials
 - **Microstructural information**, that is typically a combination of the different aspects mentioned above with at least some lateral resolution. **Imaging techniques** are usually utilized, like light optical microscopy (**LOM**, bright field, dark field, polarization microscopy, Kerr, etc.), scanning electron microscopy (**SEM**, secondary electrons, backscattered electrons, characteristic X-rays, electron backscatter diffraction), transmission electron microscopy (**TEM**, bright field, dark field, high resolution TEM).

Structural Investigations

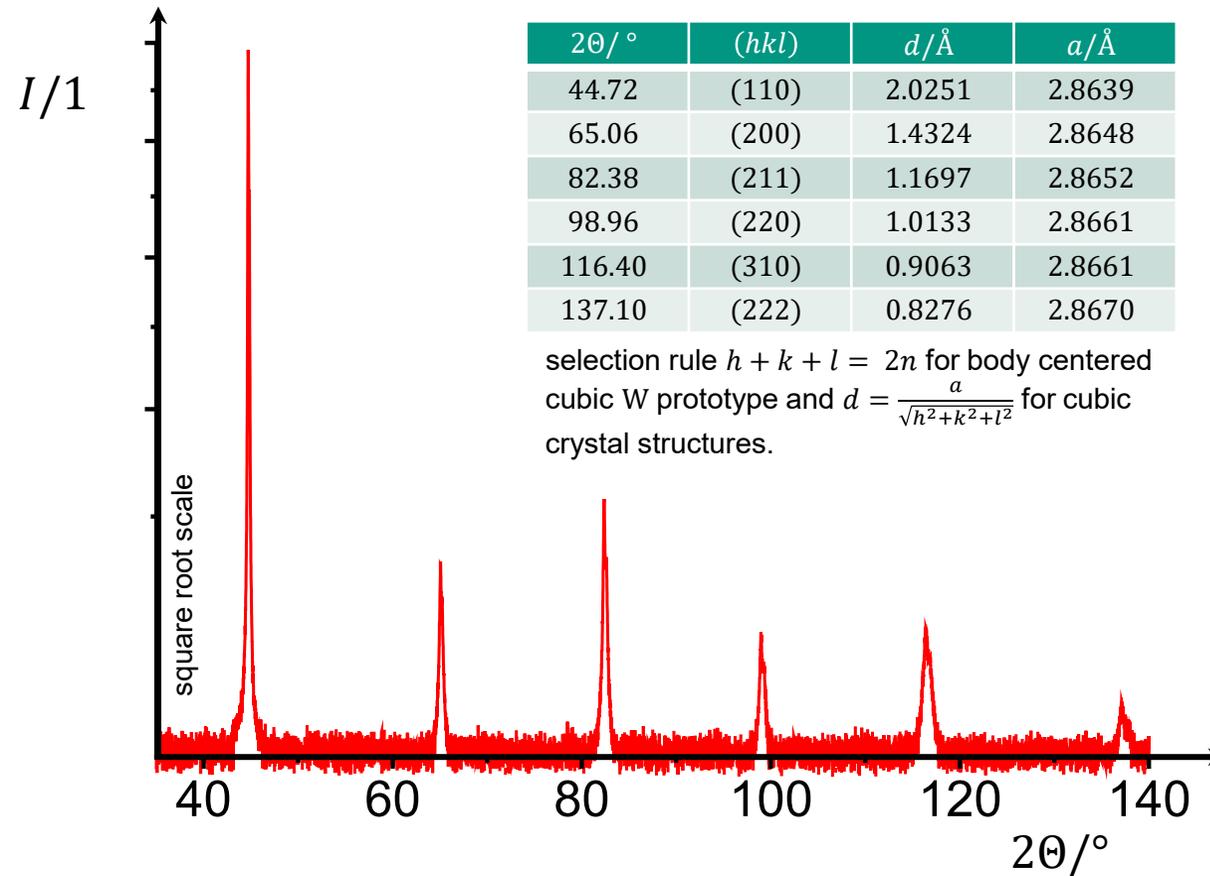
- **Diffraction techniques** rely on the **interference of beams with the lattice of crystalline materials**.
- By the analysis of **diffraction patterns (position, intensity, shape and width of peaks)**, following information can be deduced:
 - **ideal structure**:
 - type of the crystal structure (point group, space group)
 - mockup of the crystal structure (lattice parameters, occupation of lattice sites)
 - sometimes also information is available about **real structure** also:
 - lattice imperfections, like composition, dislocation density, grain size, planar faults, etc.
 - preferred orientation/texture of crystals

Structural Investigations



X-ray diffraction setup in Bragg-Brentano geometry and θ - θ focusing

Structural Investigations



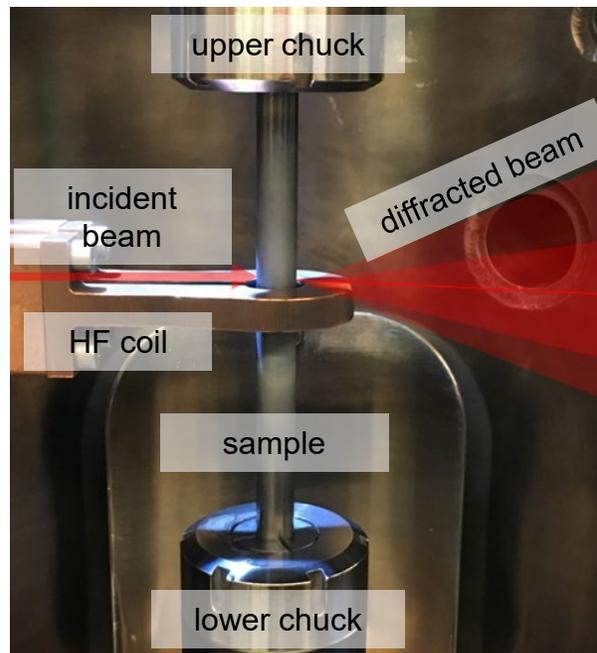
Iron α -Fe with CuK α radiation ($\lambda = 1.540598 \text{ \AA}$)

Structural Investigations

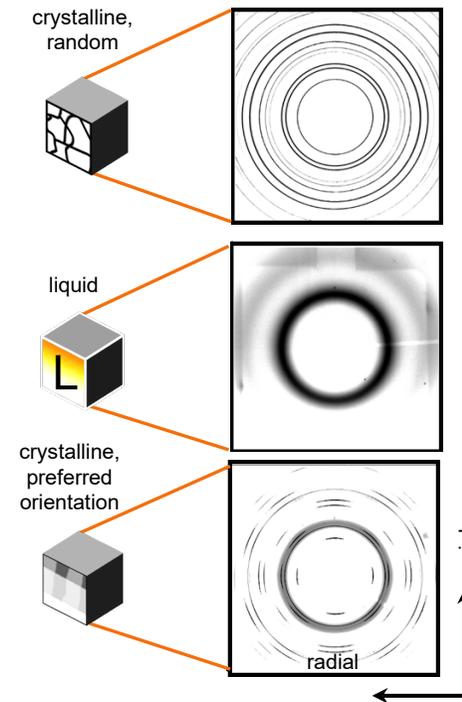
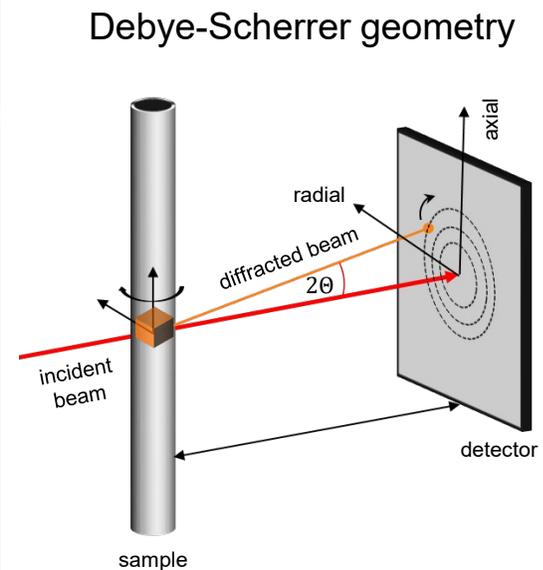
- **Lab-based** techniques typically involve rather long acquisition times. Hence, the analysis is **often** done **ex situ**. For **faster acquisition** and in situ analysis, **line detectors** (covering a range of 2θ instead of just one position) or **areal detectors** (which allow for the observation of larger sections of the diffraction cones).
- **Synchrotron** methods allow for **fast and high resolution in situ scans** during phase transformations.
- A variety of setups exists that allow for the control of external conditions, for example heating stages or furnaces. In order to establish protective atmospheres for high temperature measurements, graphite covers or inert gas purging exist.

Structural Investigations

- Directional solidification is a casting technique used to align microstructural constituents (with morphology and crystal structure) with respect to the solidification direction.
- For high temperature applications, the elimination of transversal grain or phase boundaries is useful to enhance creep resistance.



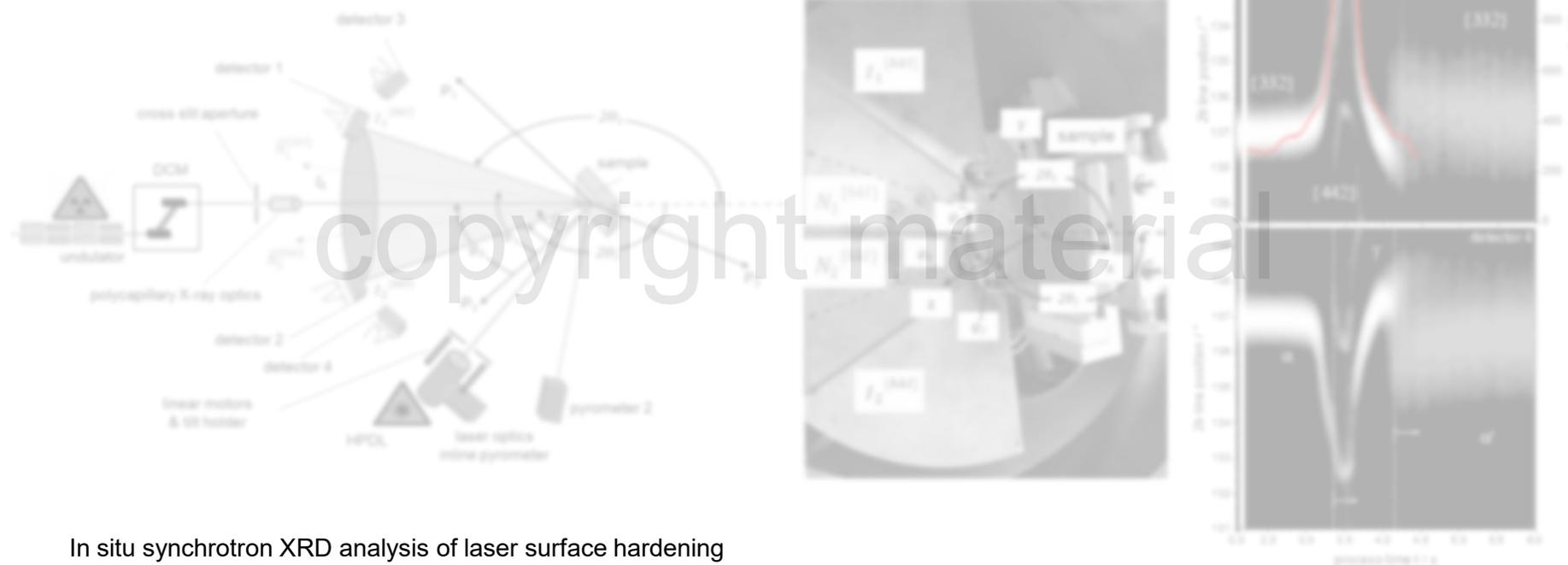
In situ observation of directional solidification by diffraction



C. Gombola et al.: A zone melting device for the in situ observation of directional solidification using high-energy synchrotron X-rays, Review of Scientific Instruments 91 (2021) 093901

Structural Investigations

- Laser surface hardening is a hardening technique to achieve high fatigue and wear resistant surfaces while maintaining a ductile core by martensitic hardening and the formation of compressive residual stresses.
- To improve and validate numerical process simulation and thereby process predictions, real time insights provide a useful tool.



In situ synchrotron XRD analysis of laser surface hardening

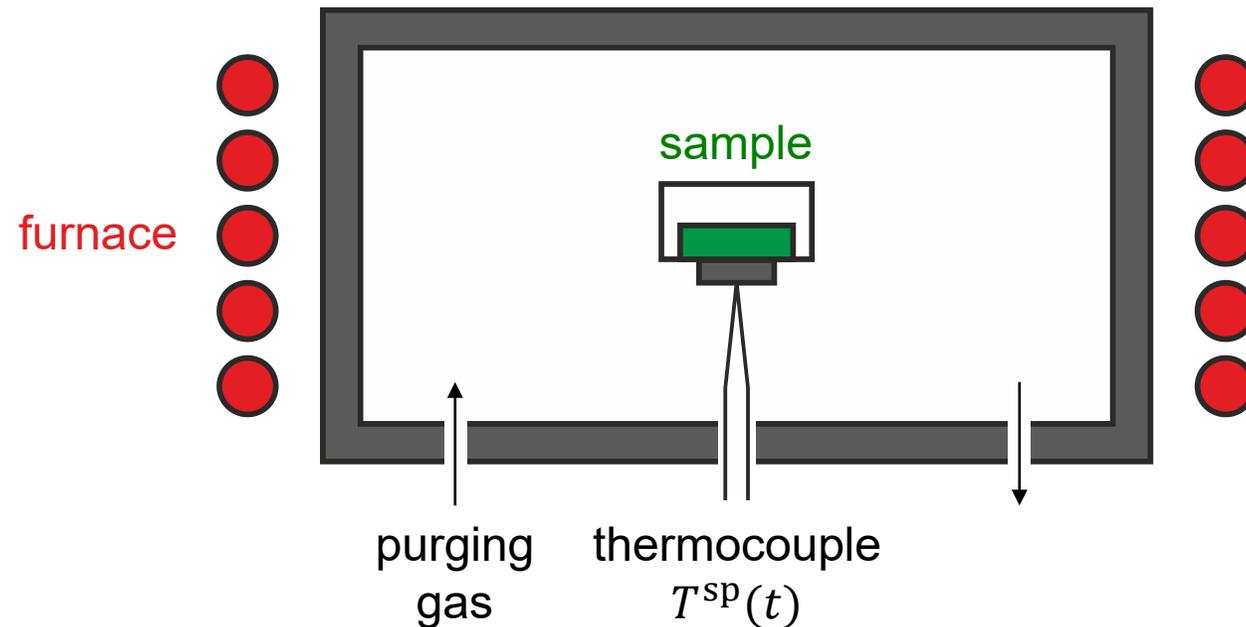
D. Kiefer et al.: Real-time stress evolution during laser surface line hardening at varying maximum surface temperatures using synchrotron X-ray diffraction, Optics & Laser Technology 140 (2021) 106964

Physical Investigations

- By far the most relevant methods to assess temperature-dependent phase transformations (which are essentially the scope of this lecture) are methods of **thermal analysis (TA)**.
- Apart from specialized methods, the commonly applied techniques are:
 - **Differential thermal analysis (DTA)**
 - **Differential scanning calorimetry (DSC)**
 - **Dilatometry**
- In some cases, the TA setups are built into synchrotron stations to obtain both, structural and physical information at the same time during the phase transformation.

Physical Investigations

■ Thermal analysis:



Physical Investigations

- Thermal analysis:
 - During phase transformations, specific heat might change as a function of temperature (continuous phase transformations, see Ch. 1a) and/or transformation heat is released or consumed (discontinuous phase transformations).
 - Hence, the temperature as a function of time $T^{\text{sp}}(t)$ of a sample during heating or cooling is indicative of a phase transformation.

Gibb's Phase Rule

- For a **thermodynamic system** composed of P **phases** and C **components** in **thermodynamic equilibrium**, there is only a limited number of **degrees of freedom** F . F denotes the number of variables that can be changed without a phase transformation taking place.
- Each phase in the system is described by $C - 1 + 2$ independent variables:
 - $1 \times$ Temperature T^j
 - $1 \times$ Pressure p^j
 - $(C - 1) \times$ Chemical composition: x_A^j, x_B^j, \dots
(the composition of the remainder component is not independent due to $\sum_i x_i^j = 1$)
- For P phases, this yields **in total $P(C + 1)$ independent variables.**

Gibb's Phase Rule

- **Thermodynamic equilibrium** (see Ch. 1b) is obtained with:
 - **Thermal equilibrium:** $T^\alpha = T^\beta = \dots (P - 1)$
 - **Hydrostatic equilibrium:** $p^\alpha = p^\beta = \dots (P - 1)$
 - **Chemical equilibrium:** $\mu_A^\alpha = \mu_A^\beta = \dots, \mu_B^\alpha = \mu_B^\beta = \dots, \dots C(P - 1)$

- The chemical potential is $\mu_i^j = \left. \frac{\partial G^j}{\partial N_i} \right|_{T^j, p^j}$. **Hence, it corresponds to a change in G when atoms are removed or added to a phase.** When phases are in contact, it corresponds to a flux from one phase to another. If there is a decrease in G , there is a driving force for diffusion and the flux will persist. When G remains constant, no driving force for diffusion exists and the system is in chemical equilibrium – over long times no changes occur.

- There are $(P - 1) + (P - 1) + C(P - 1) = (P - 1)(C + 2)$ **conditions** restricting F over the number of independent variables.

Gibb's Phase Rule

■ Hence,

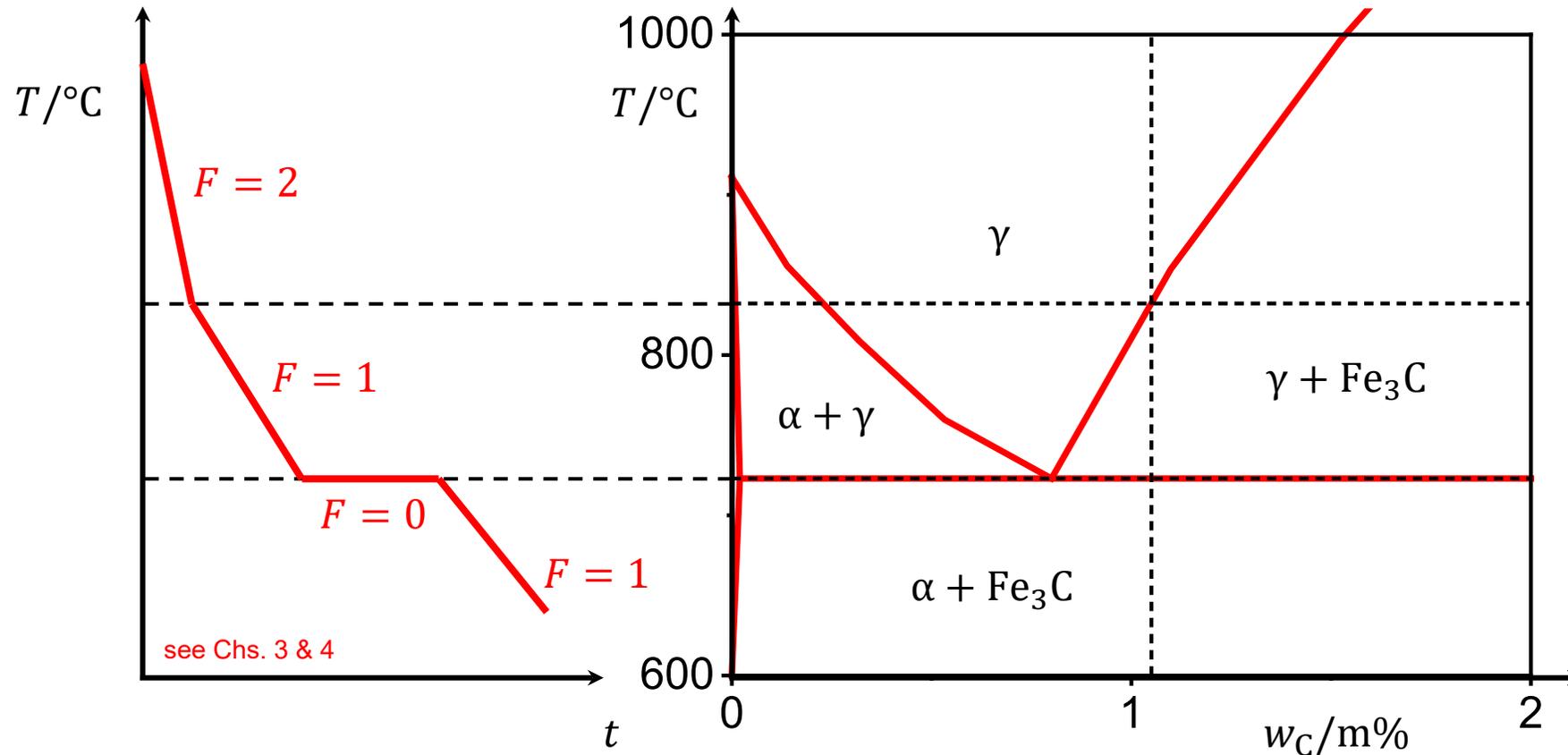
$$F = P(C + 1) - (P - 1)(C + 2)$$
$$F = C - P + 2$$

■ When $p = \text{const.}$,

$$F = C - P + 1$$

Physical Investigations

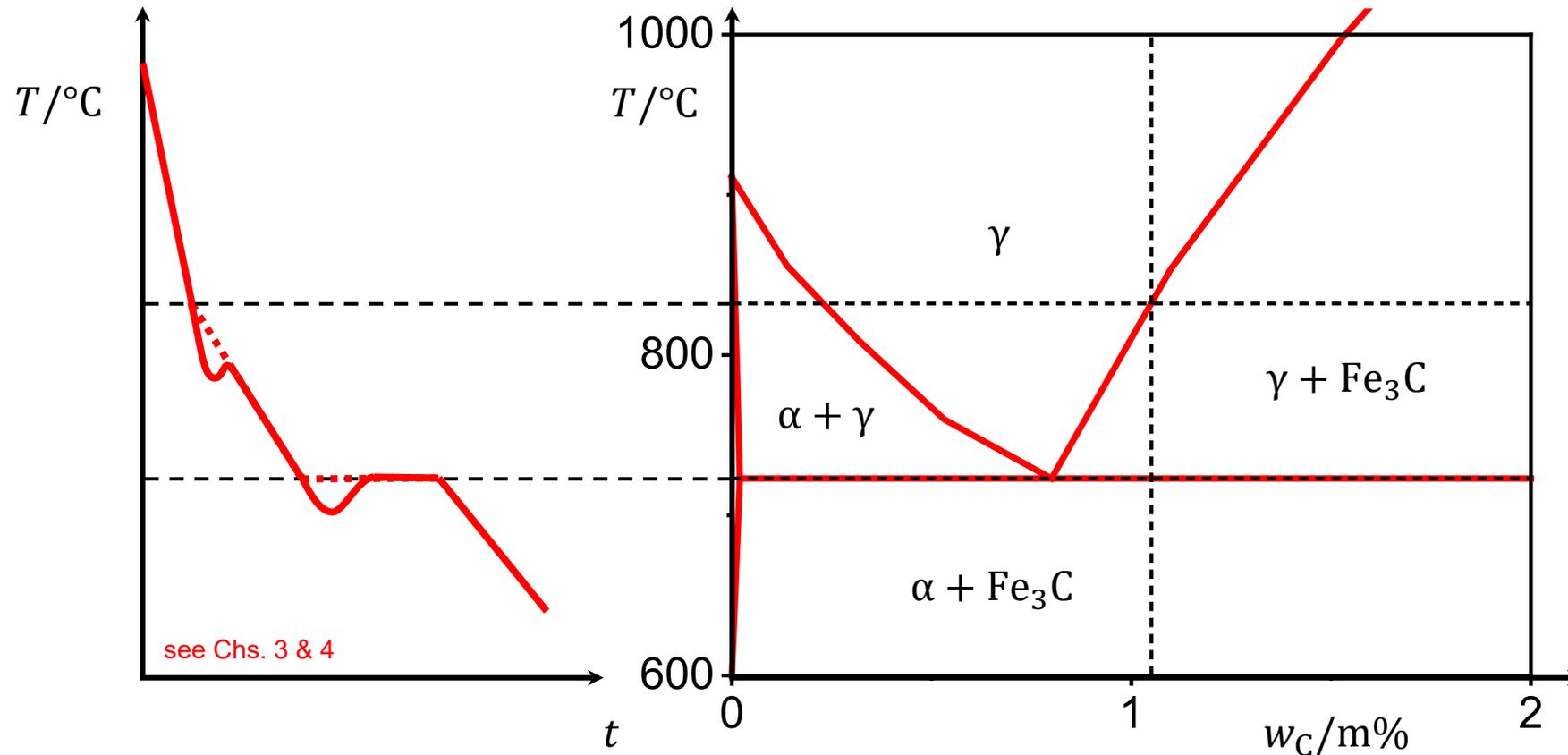
■ Thermal analysis:



C105 plain steel during free cooling considering heat release only

Physical Investigations

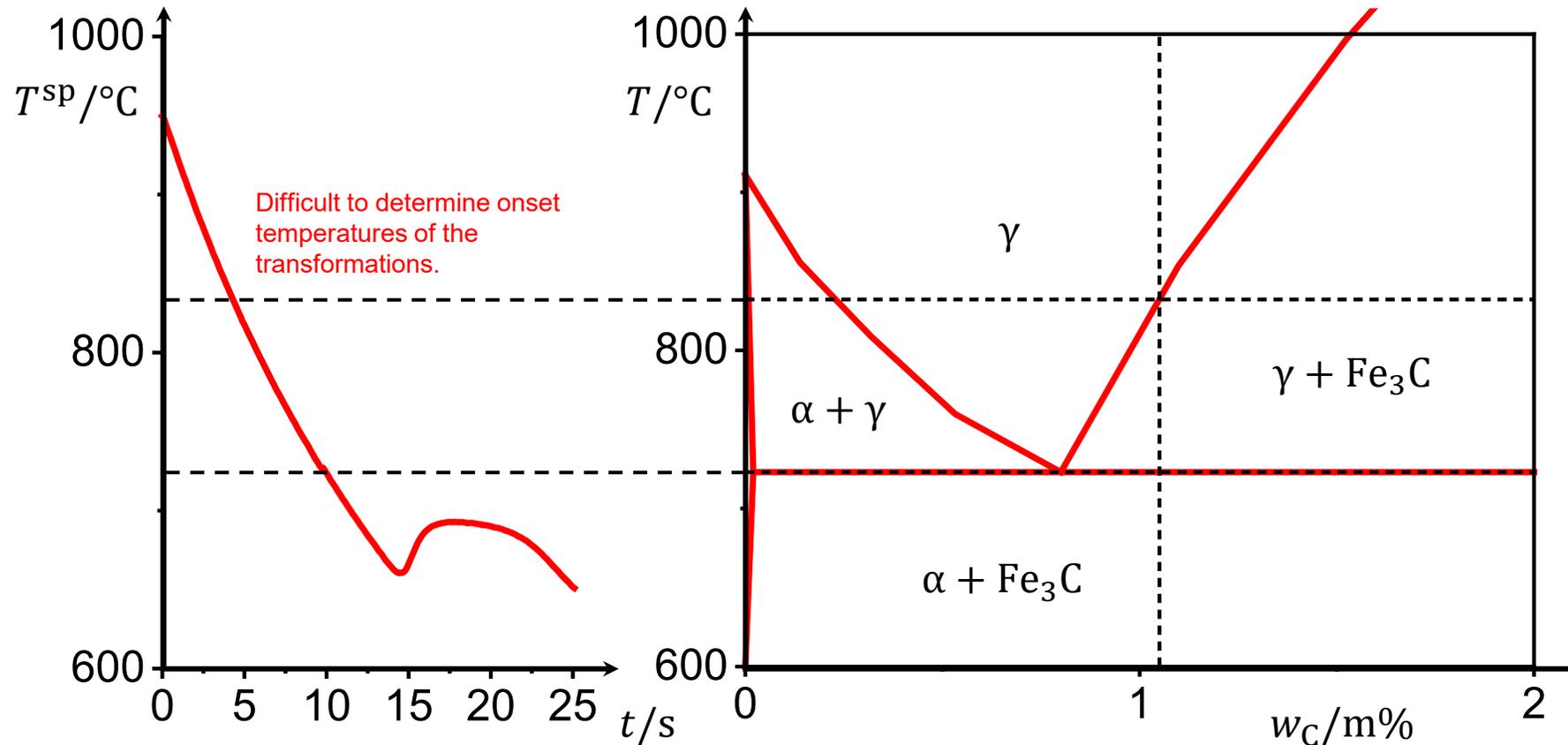
■ Thermal analysis:



C105 plain steel during free cooling considering heat release and super cooling

Physical Investigations

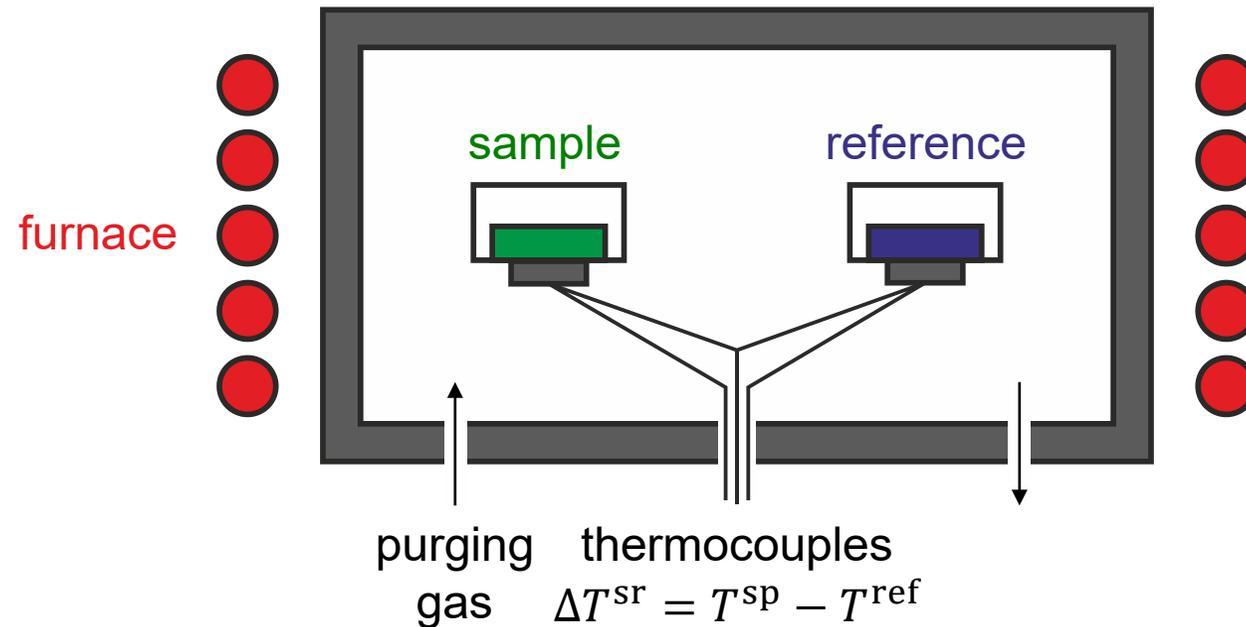
■ Thermal analysis:



C105 plain steel during free cooling, experimental result

Physical Investigations

- Differential thermal analysis:

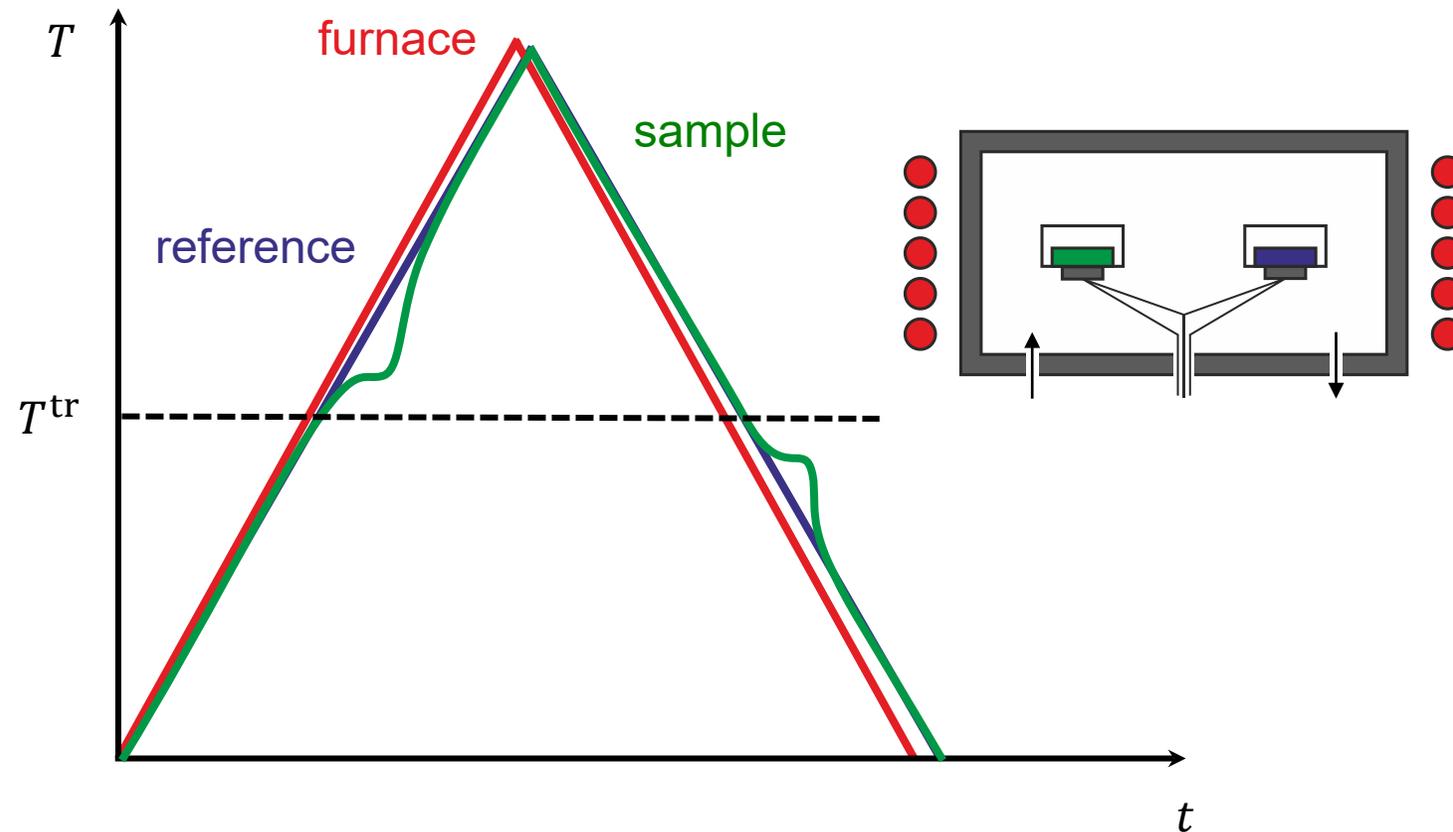


Physical Investigations

- Differential thermal analysis:
 - In order to improve sensitivity, the temperature difference ΔT^{sr} of a sample to a reference material can be obtained.
 - This allows for better observation of changes in heat capacity and changing specific heat.

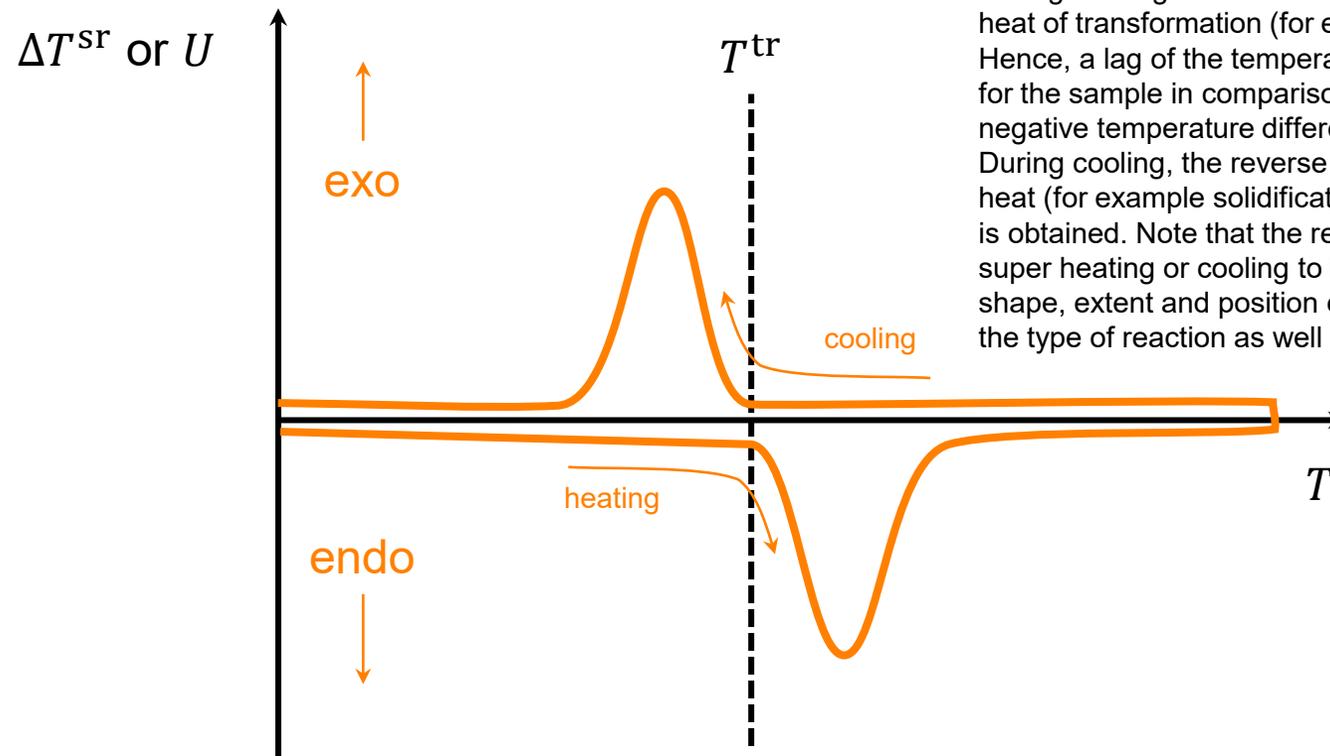
Physical Investigations

- Differential thermal analysis:



Physical Investigations

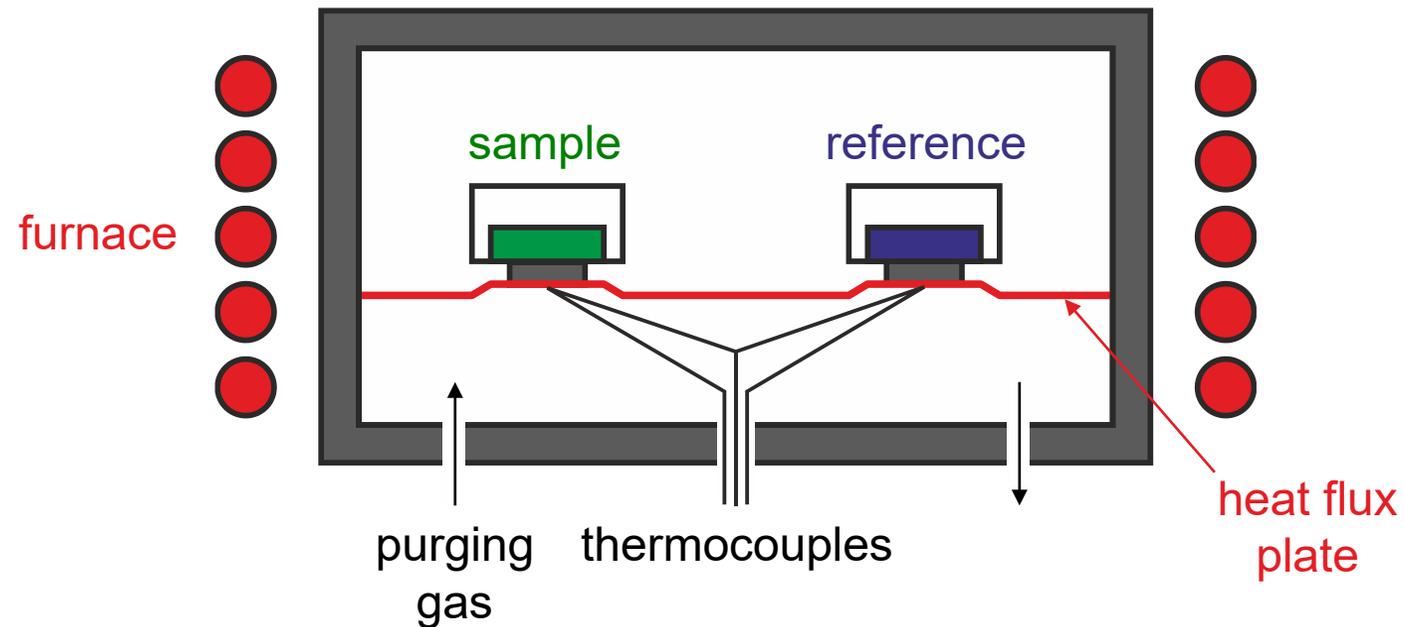
■ Differential thermal analysis:



During heating an endothermic reaction requires a heat of transformation (for example during melting). Hence, a lag of the temperature increase is obtained for the sample in comparison to the reference and a negative temperature difference ΔT^{sr} is detected. During cooling, the reverse reaction might release heat (for example solidification) and a positive signal is obtained. Note that the reaction require sufficient super heating or cooling to initiate. The onset, shape, extent and position of the peak depend on the type of reaction as well as its kinetics.

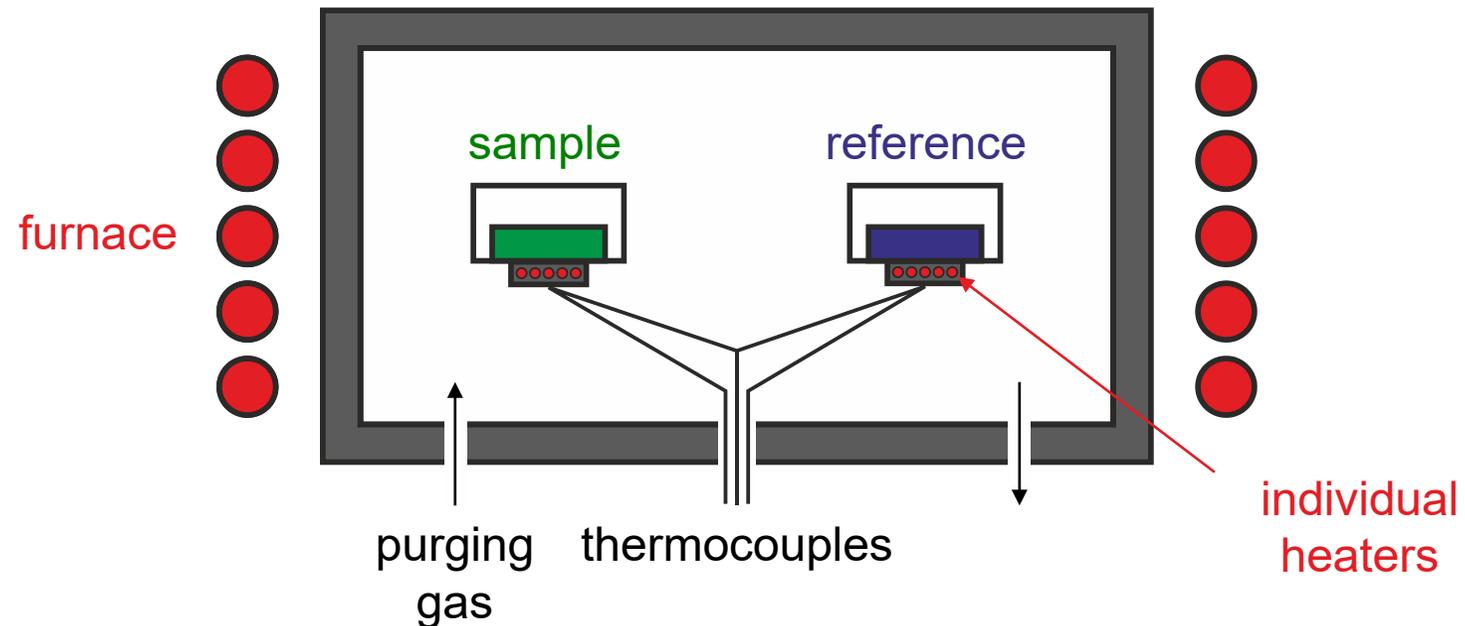
Physical Investigations

- Differential scanning calorimetry:



Physical Investigations

- Differential scanning calorimetry (power-compensated):



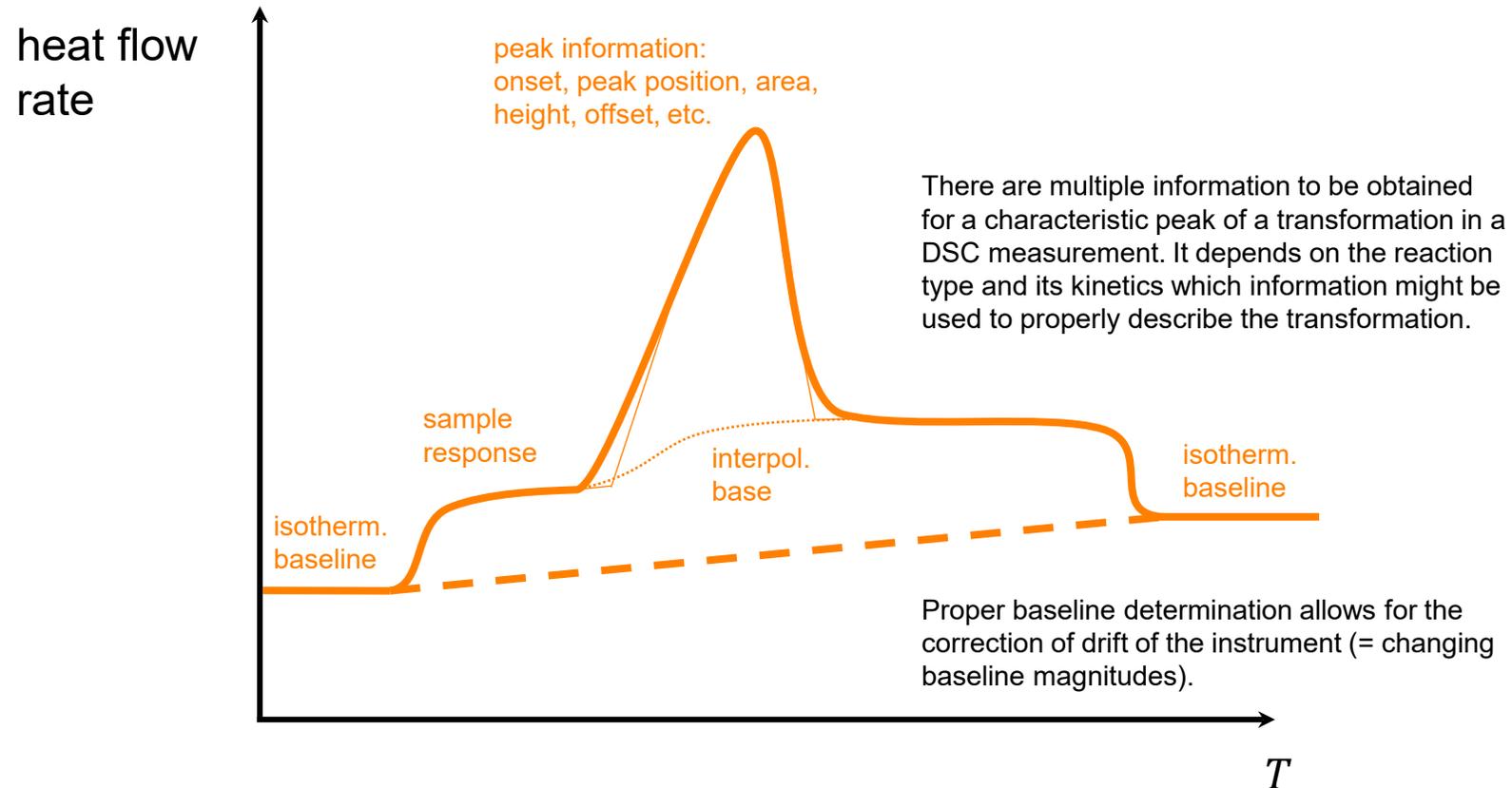
Physical Investigations

- Differential scanning calorimetry (power-compensated):
 - In a DSC experiment, the difference in heat flow rate to the sample and the reference is detected while both are subjected to the temperature program.
 - For the heat flux DSC setup, the temperature difference between the sample and reference is detected similar to a DTA experiment. The heat flux plate allows for coupling of the two and also allows for the experiment to be calibrated to estimate the heat flow rate (the latter possibility is the essential difference from the DTA setup which cannot be calibrated).
 - In a power-compensated DSC, the temperature difference between sample and reference is kept minimum by a loop control program. The power needed to maintain this condition correlates to the difference in heat flow rate to the sample and reference.

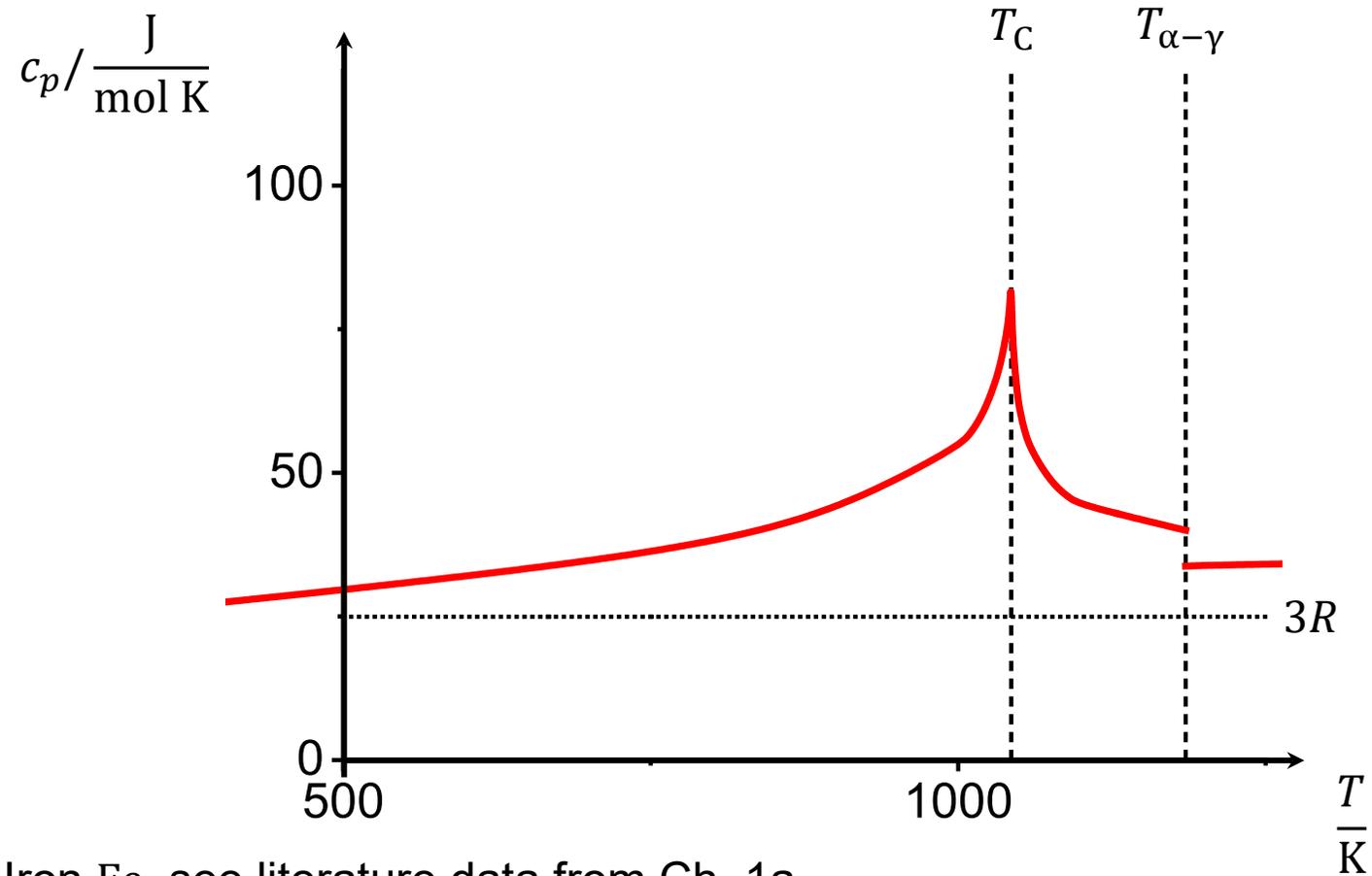
Physical Investigations

- Differential scanning calorimetry (power-compensated):
- By comparing the recorded signal of the sample to a reference measurement on a sample with known heat capacity (for example sapphire) with the identical temperature profile, $\frac{\partial H}{\partial T} \Big|_p$ of a sample can be obtained.
- Hence, temperature-dependent c_p and heats of transformation ΔH^{tr} can be obtained.

Physical Investigations



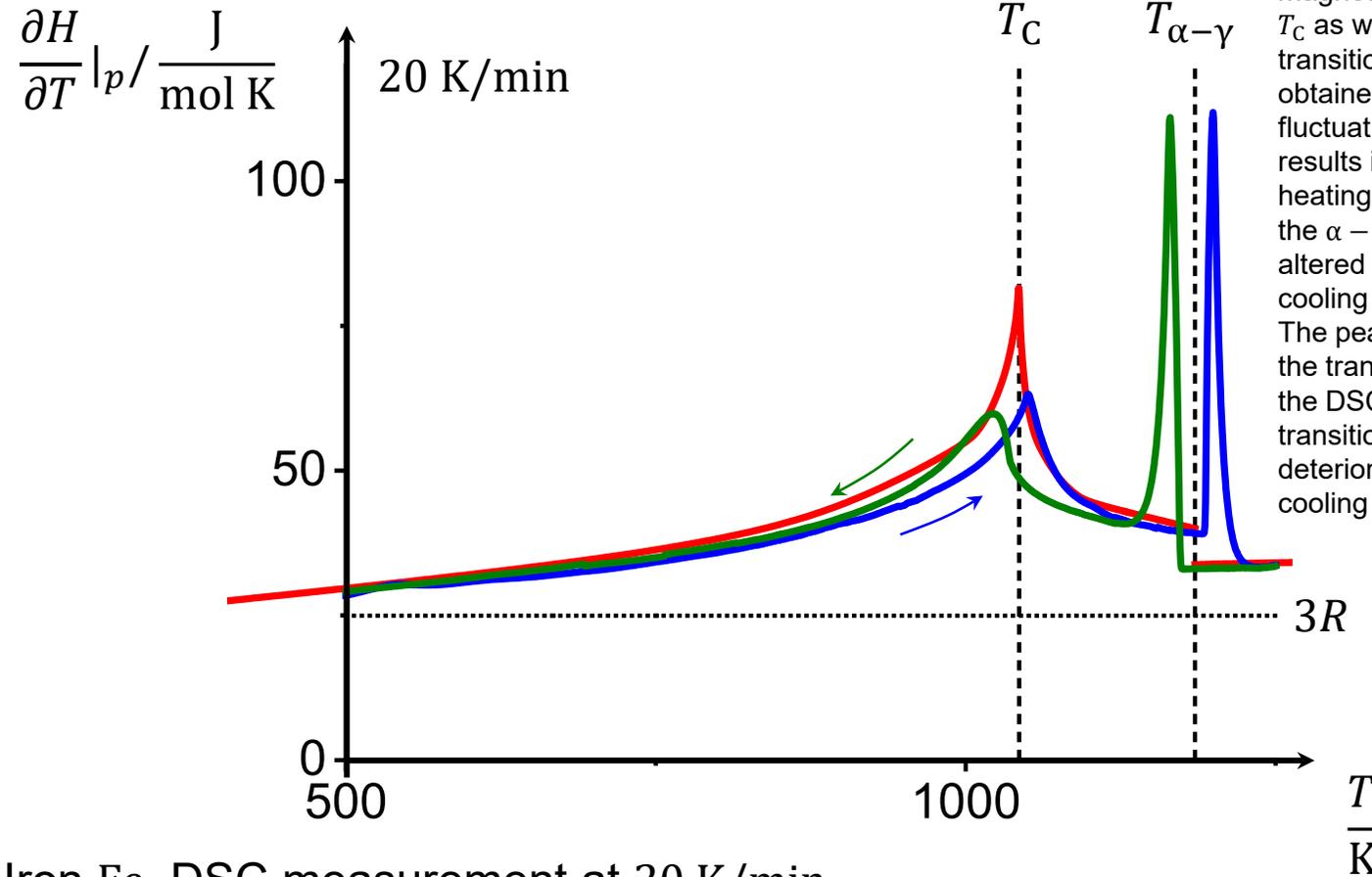
Physical Investigations



Iron Fe, see literature data from Ch. 1a

P. D. Desai: Thermodynamic Properties of Iron and Silicon, Journal of Physical and Chemical Reference Data 15 (1986) 967

Physical Investigations



Both, the anomaly of c by the magnetic transition in the vicinity of T_C as well as the structural transition between α and γ are obtained. The occurrence of fluctuations above and below T_C results in deviations of c at finite heating/cooling rate. The onsets of the $\alpha - \gamma$ transformation are altered by super heating and cooling for initiation of nucleation. The peak areas are indicative of the transformation heats. Note that the DSC signal exhibits a zero transition upon cooling that usually deteriorates the validity of the cooling curve.

Iron Fe, DSC measurement at 20 K/min

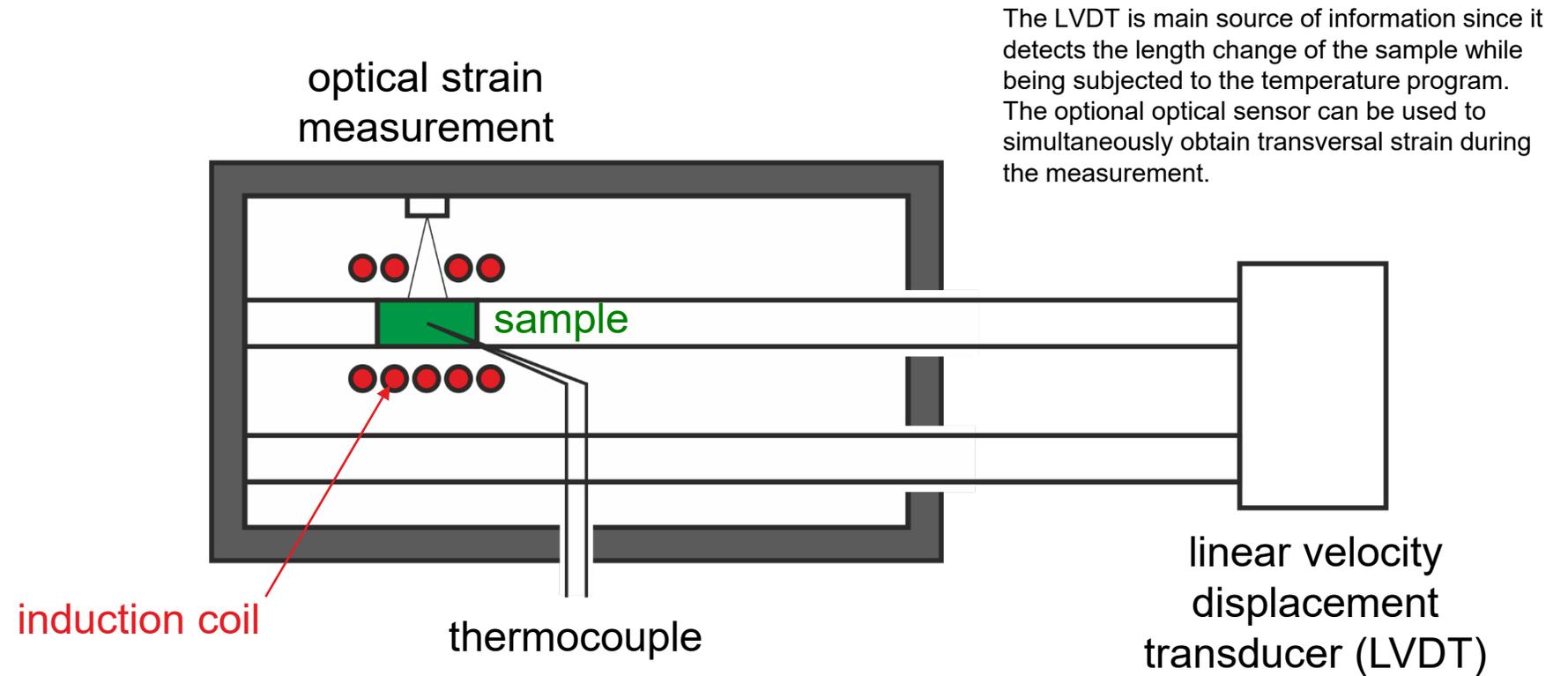
P. D. Desai: Thermodynamic Properties of Iron and Silicon, Journal of Physical and Chemical Reference Data 15 (1986) 967

Physical Investigations

- In case of a DSC experiment (independent of the measurement with respect to reference substance just for the conversion of $\frac{V}{g}$ to $\frac{W}{g}$), the setup needs to be calibrated based on suitable reactions with known transformation heats (typically melting of substances, like In, Bi, Sn, Zn, Al, etc.).
- For reference measurements to determine c_p , baseline acquisition (empty chamber and pans), sample measurement and reference measurement need to be done (hence, at least three individual DSC runs are needed under identical conditions).
- In order to improve accuracy, thermal resistance (unit of K/W) of the sample and the reference need to be adjusted and proper contact of the samples with the pans is required. In addition, gas flow through the pans and lids is not trivial and needs to be optimized in some cases.
- In case of reactive materials, matching pan materials need to be selected (Pt, Pt with Al_2O_3 inserts, Au, Y_2O_3 , etc.) in order to avoid impact of reaction heats on the DSC signal.
- In case of significant oxidation (associated with reaction heat), purification of the protective atmosphere needs to be done (for example Zr getter in the gas stream).

Physical Investigations

■ Dilatometry:



Physical Investigations

- Dilatometry:
- Materials exhibit thermal expansion as a function of temperature as a result of anharmonicity of the binding potential. At high temperatures, strong non-linearity is induced by vacancy formation. When structural transformations occur, the specific volume might change and the shape change of the sample can be obtained.
- The shape change can be obtained with high acquisition rate (no thermal lag or equilibration needed). In conjunction with induction heating systems and gas purging through the sample, much higher heating and cooling rate can be established than with other thermal analysis techniques. Hence, dilatometry is suited not only for investigation of reconstructive but also displacive and intermediate transformations (for example perlite, martensite or bainite formation).

Physical Investigations

■ Dilatometry:

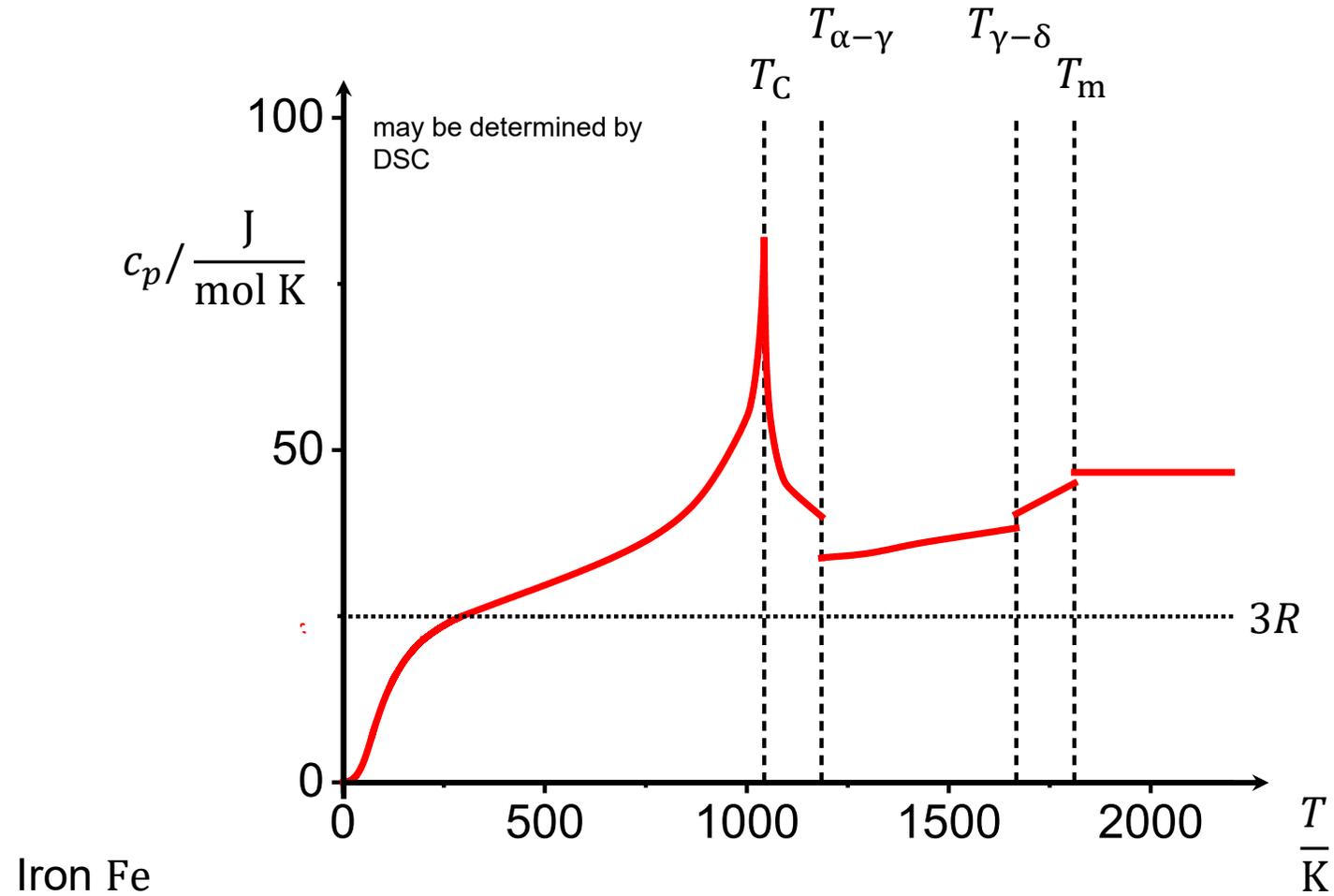
$$V = (L_0 + \Delta L)^3 = L_0^3 + 3 L_0^2 \Delta L + 3 L_0 \Delta L^2 + \Delta L^3 \approx L_0^3 + 3 L_0^2 \Delta L$$

$$\Delta V = V - L_0^3 \approx 3 L_0^2 \Delta L$$

$$\frac{\Delta V}{V_0} \approx 3 \cdot \frac{\Delta L}{L_0}$$

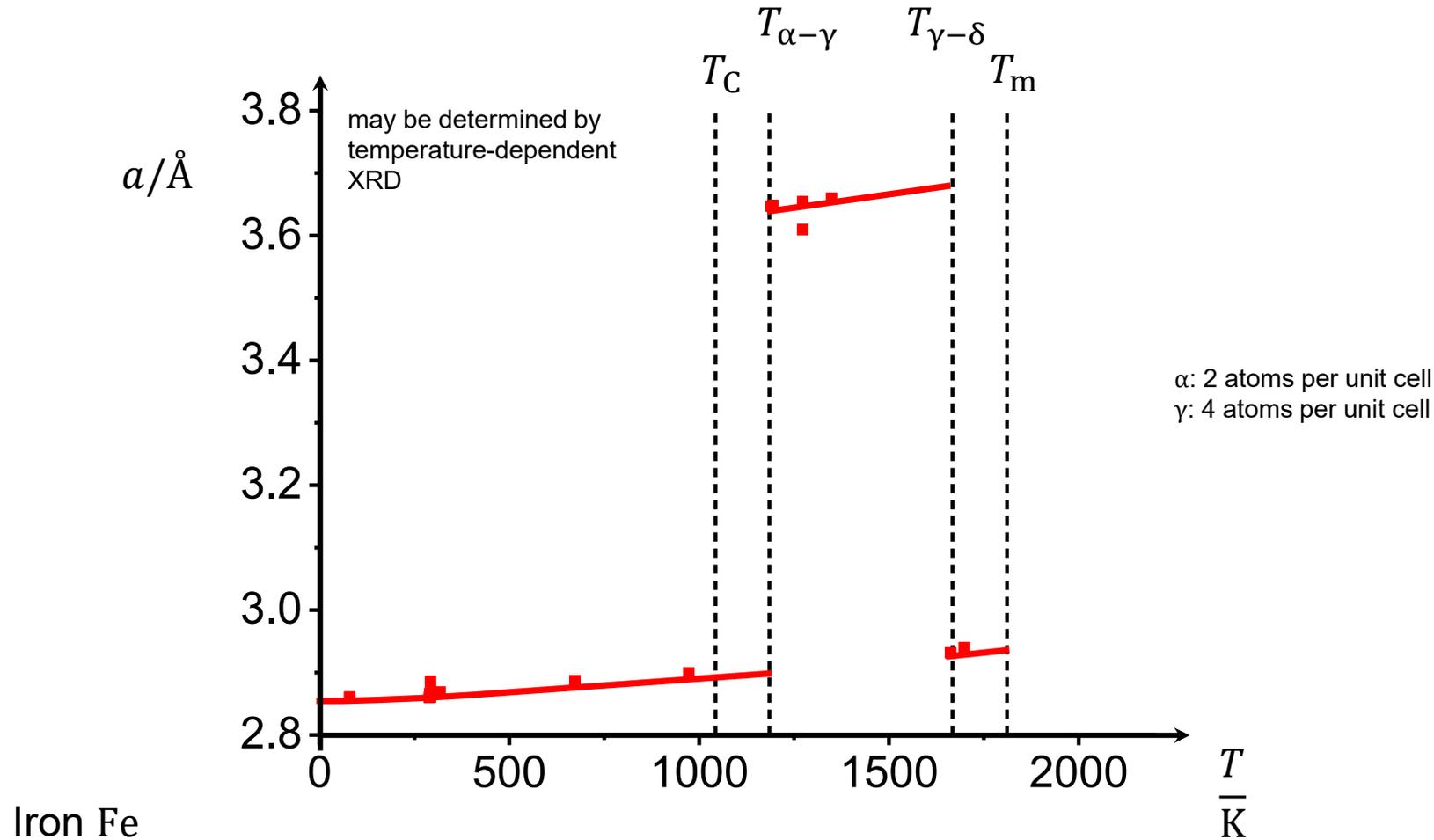
Note that a change in volume due to a transformation correlates to a change in length.

Physical Investigations



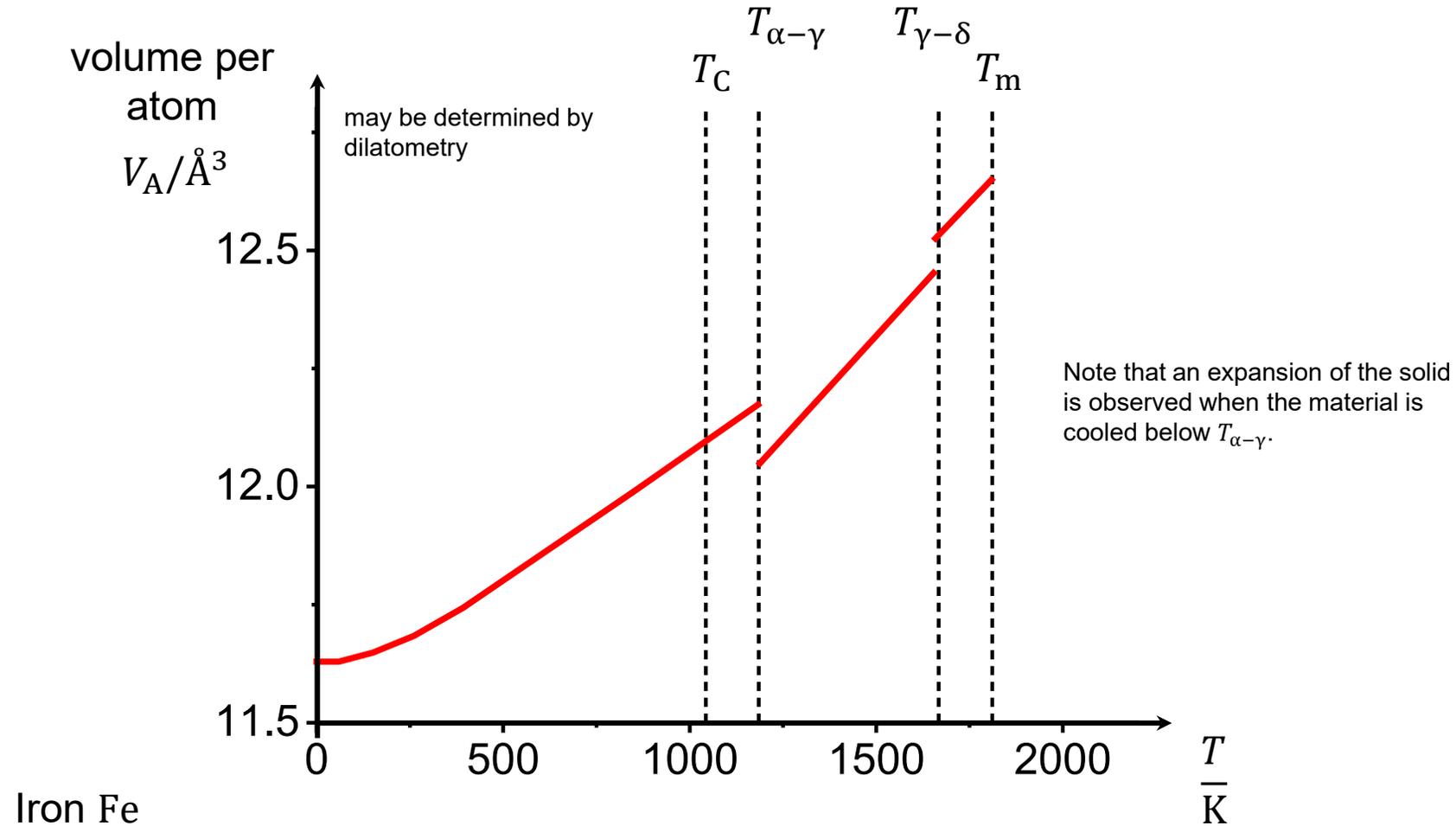
P. D. Desai: Thermodynamic Properties of Iron and Silicon, Journal of Physical and Chemical Reference Data 15 (1986) 967

Physical Investigations



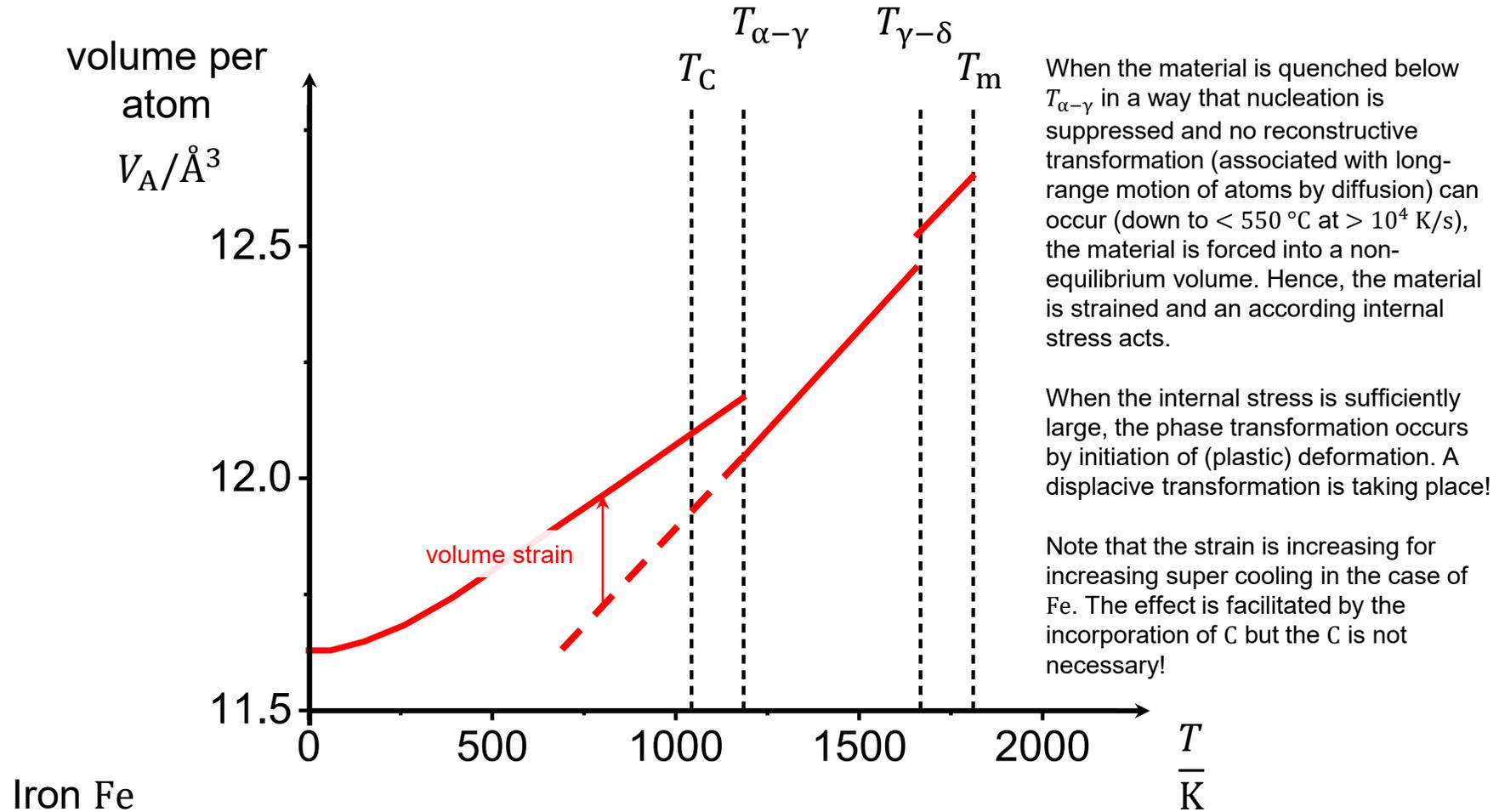
H.K.D.H. Bhadeshia and R.W.K. Honeycombe: Steels - Microstructure and Properties, Amsterdam, Boston, etc.: Elsevier, Butterworth-Heinemann (2006)
 various datasets from <https://icsd.fiz-karlsruhe.de/> database

Physical Investigations



H.K.D.H. Bhadeshia and R.W.K. Honeycombe: Steels - Microstructure and Properties, Amsterdam, Boston, etc.: Elsevier, Butterworth-Heinemann (2006)

Physical Investigations



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Chemical and Microstructural Investigations

- Chemical and microstructural investigation:
- Qualitative chemical information can be obtained in **scanning electron microscopes** (SEM) by imaging of **backscattered electron** (BSE) since backscattering coefficient depends on **average atomic number Z** within the probe volume.
- Locally resolved, quantitative chemical information can be obtained by various methods. Most importantly, **energy-dispersive X-ray spectroscopy** (EDX, EDS) or **wavelength-dispersive X-ray spectroscopy** (WDX, WDS) are applied in materials science; usually in conjunction with imaging in the SEM or **transmission electron microscope** (TEM).

Microstructural Investigations

- Microstructural investigations:
- Locally resolved crystallographic information can be obtained by means of **electron backscatter diffraction** (EBSD) in the SEM or **selected area diffraction** (SAD) in the TEM.
- The acquisition times scale roughly as follows:
 - Secondary electron imaging (SEM-SE, topography information)
 - Backscatter electron imaging (SEM-BSE)
 - Bright field, dark field, diffraction imaging (TEM-BF/DF/SAD)
 - Orientation imaging by electron backscatter diffraction (SEM-EBSD)
 - Energy-dispersive X-ray mapping (SEM-EDX)

