The Influence of Magnetic Order to Crystal Nucleation

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Overview

I Motivation

1 Thermodynamics of Undercooled Metallic Melts

2 Classical Nucleation Model

3 Magnetic Influence on Nucleation

II Thermomagnetic Analyses

1 Method of Measurement

2 Experiments on **Co**, **Co-Pd** and **Co-Au**

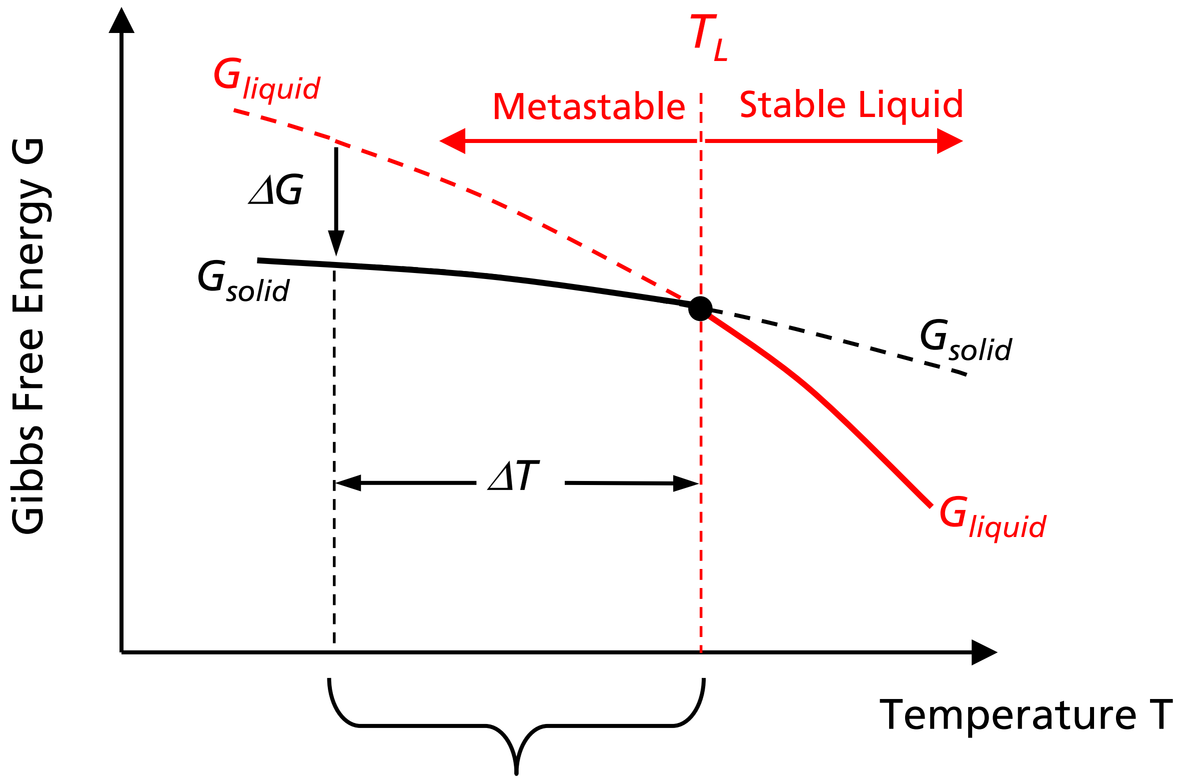
III Résumé

1 Experimental Results

2 Modification of Existing Classical Nucleation Model

1^{st} Order Phase Transition: Solid ⟷ Liquid

Driving Force to Nucleation → $\Delta G(p,T) = G_{liquid} - G_{solid}$

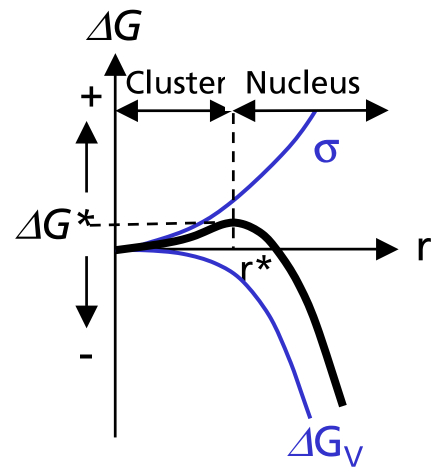


Metastable Regime of Undercooled Liquid

Motivation

Activation Energy for Nucleation:

$$\Delta G^* = \frac{16}{3}\pi \cdot \frac{\sigma^3}{(\Delta G_V)^2}$$



Gibbs Free Energy Difference

$$\Delta G_V = \frac{G^L - G^S}{V_{mol}}$$

Solid-Liquid Interfacial Energy

$$\sigma(T) = \alpha \cdot \frac{\Delta S_f \cdot T}{(N_A \cdot V_{mol}^2)^{1/3}}$$

[Spaepen, Acta Metall. **23**, (1975) 729]

Crystal Nucleation Rate: $I_{SS} = k_V \bullet e^{-f(\theta)\cdot\frac{\Delta G^*}{k_B T}}$

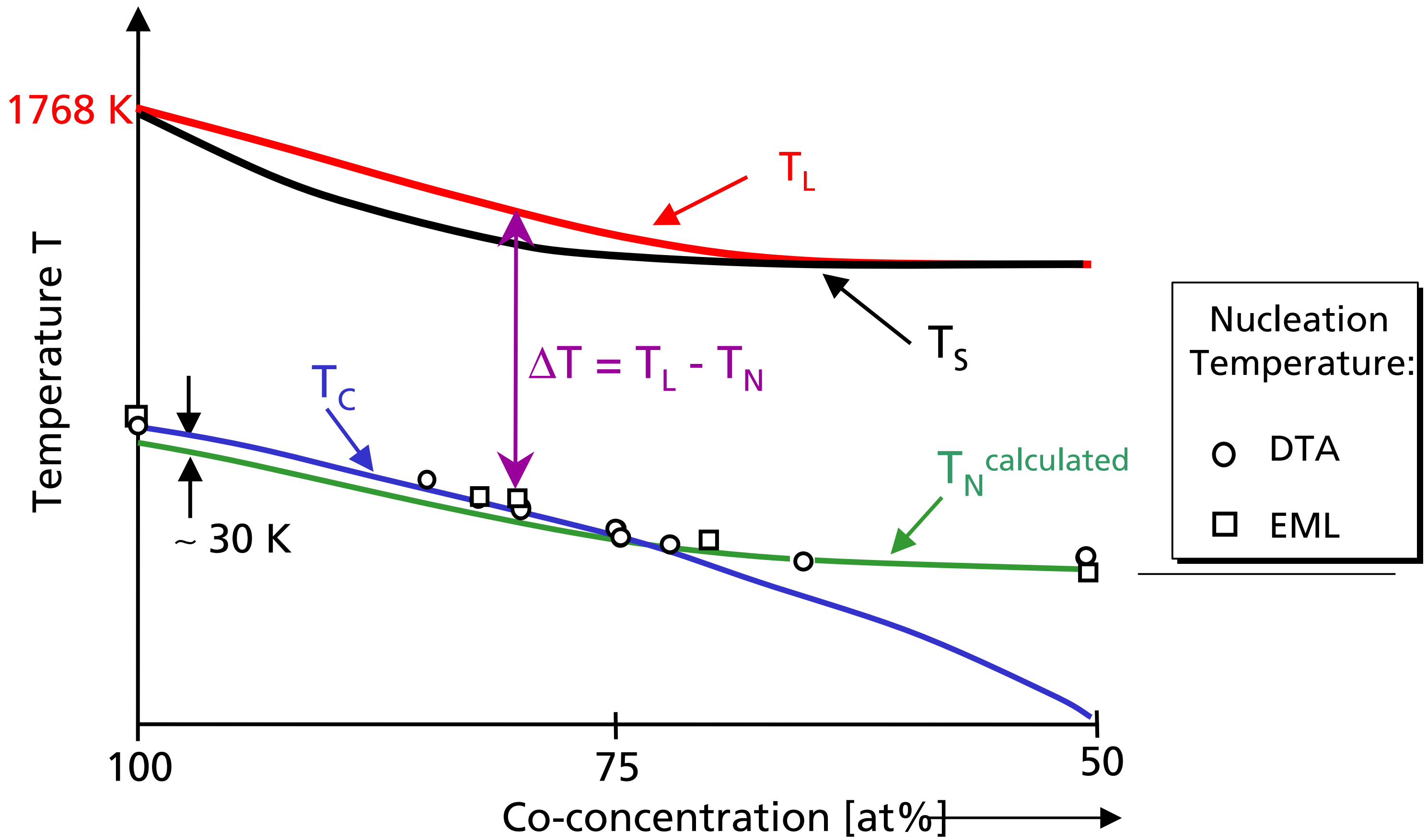
Nucleation Event: $I_{SS}(T_N) \cdot V \cdot t_N \geq 1$

Motivation

Undercooling of **Co-Pd** Alloys by Different Processing Techniques:

Differential **T**hermal **A**nalysis [Wilde, PhD-thesis, Technical University Berlin (1997)]

Electro**m**agnetic **L**evitation [Herlach et al., J.Non-Cryst.Sol. **250-252** (1999) 271]

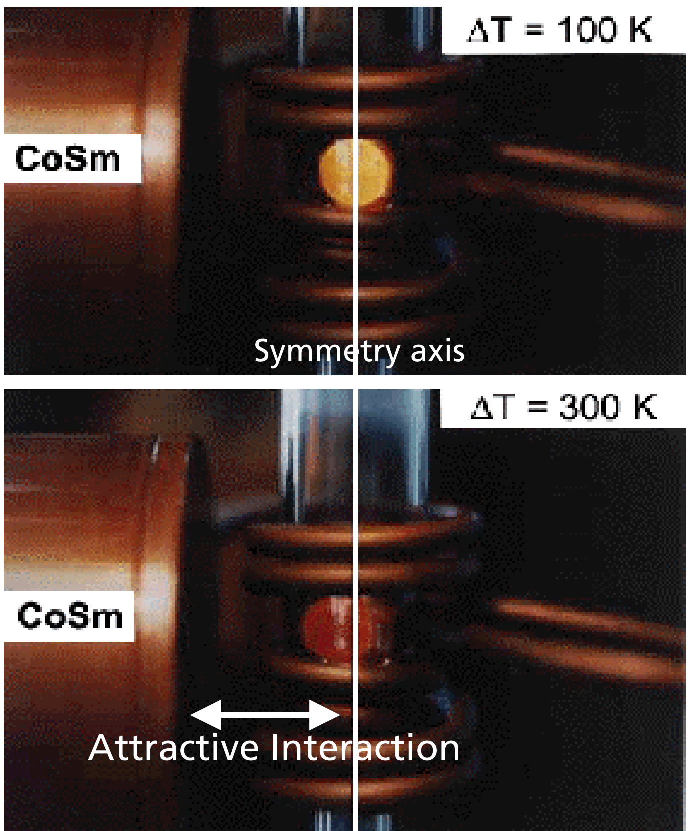


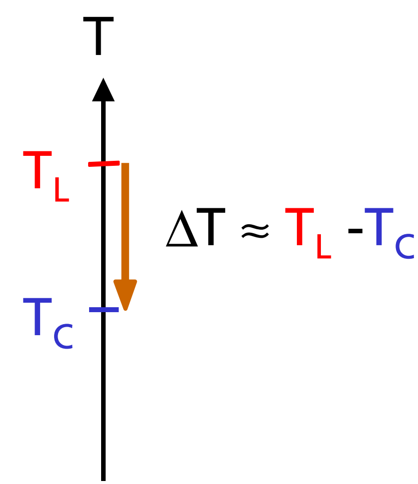
Electromagnetic Levitation of **Co-Pd** Melts

Nucleation Statistics → Observation of Magnetically Induced Crystallisation

[Schenk et al., Europhys. Lett. **50**, 3, (2000), 402]

[Holland-Moritz et al., MRS Proceedings **580**, (2000), 393]



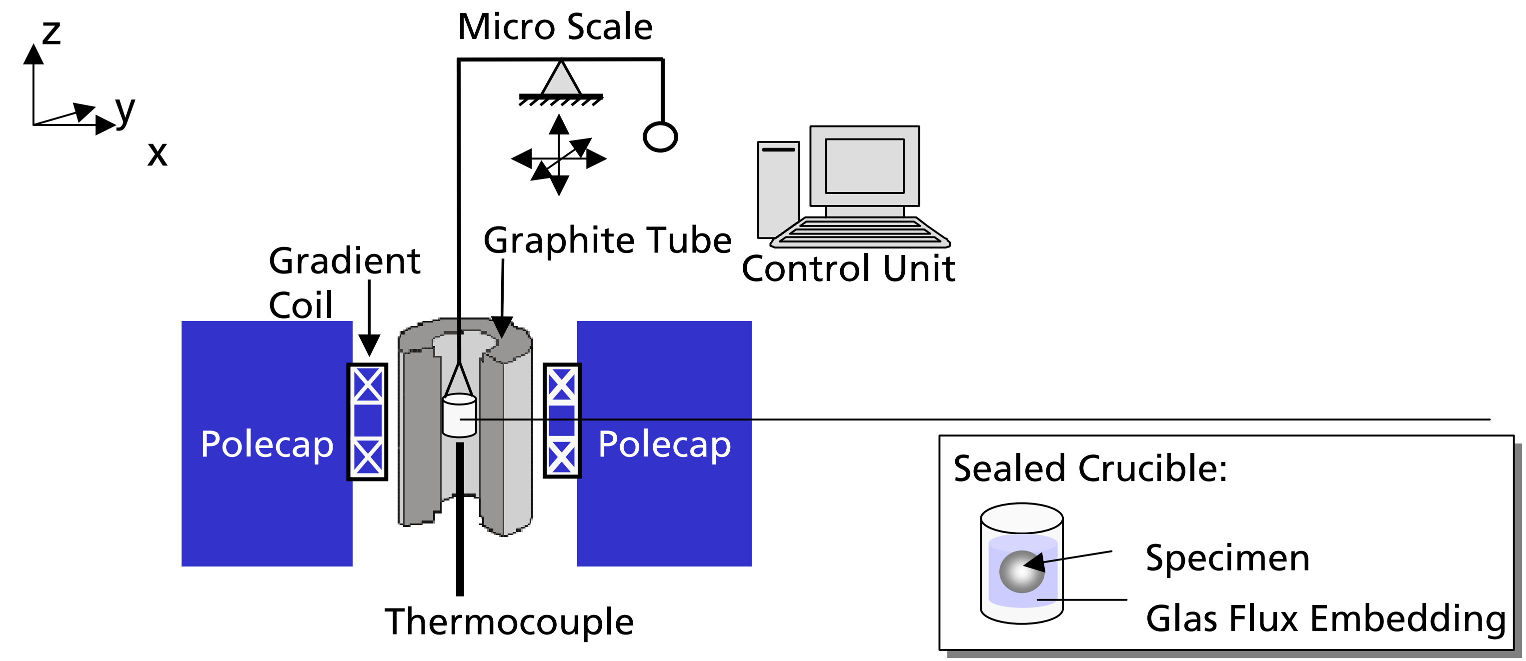


Increase of Magnetic Order while Approaching Curie-Temperature T_C!

[Platzek et al., Appl. Phys. Lett., 65 (1994) 1723]

Sketch of Constructed Faraday-Balance

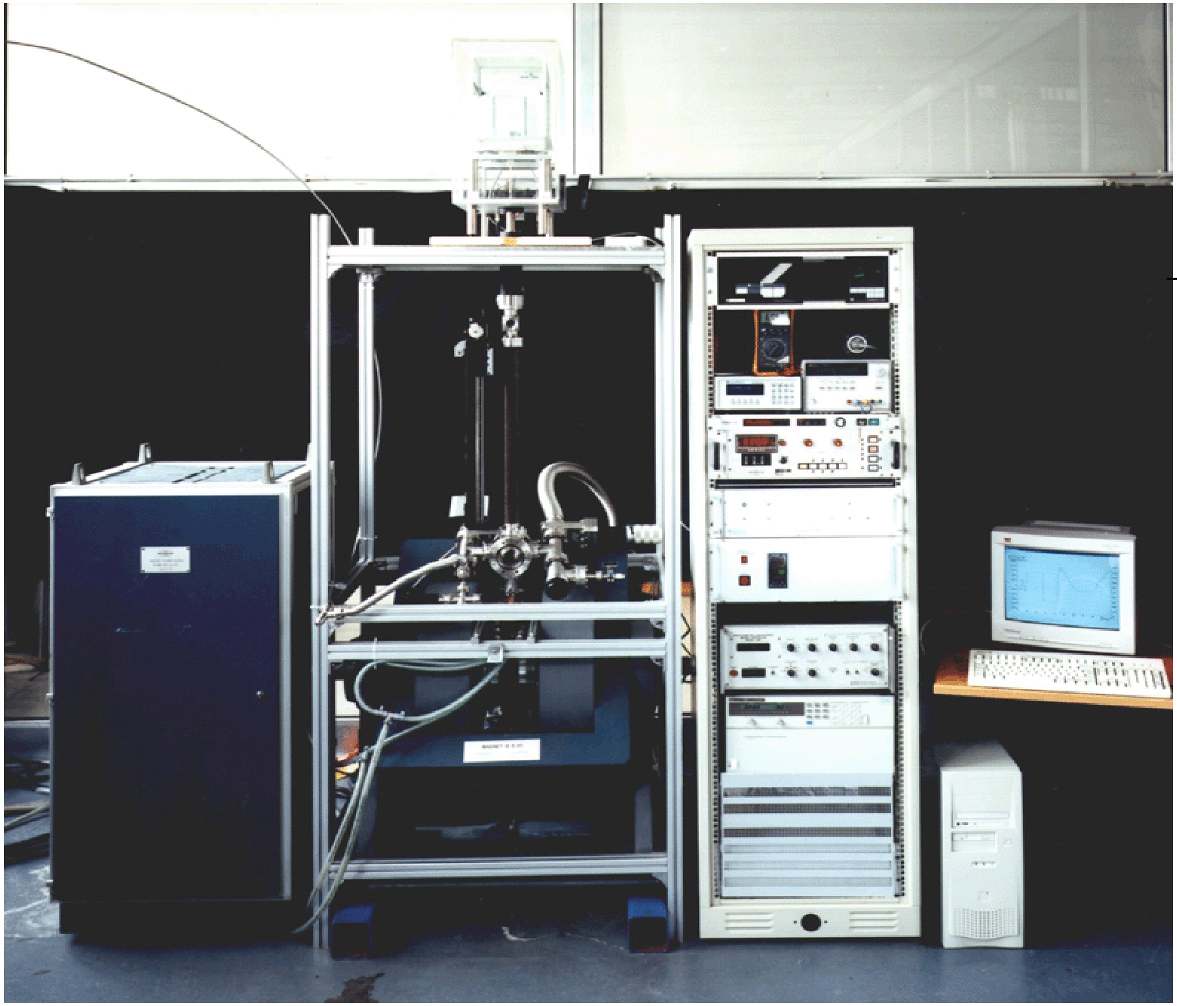
[Reutzel, Herlach, Adv. Eng. Mat. **3**, 1-2, (2001), 65]



Magnetic Force Equation

$$F_Z(T) = \mu_0 \cdot \underbrace{\rho \cdot V}_{\text{const.}} \cdot \underbrace{H_0 \cdot \frac{\partial H}{\partial z}}_{\text{const.}} \cdot \chi(T)$$

Front View of Constructed Faraday-Balance



Technical Data:

Resolution
2 µg at 20 g Load

Temperature Range
300 K < T < 2000 K

Magnetic Field
H ≤ 1.2 T

Calibration on **Cobalt**

Molecular Field Theory

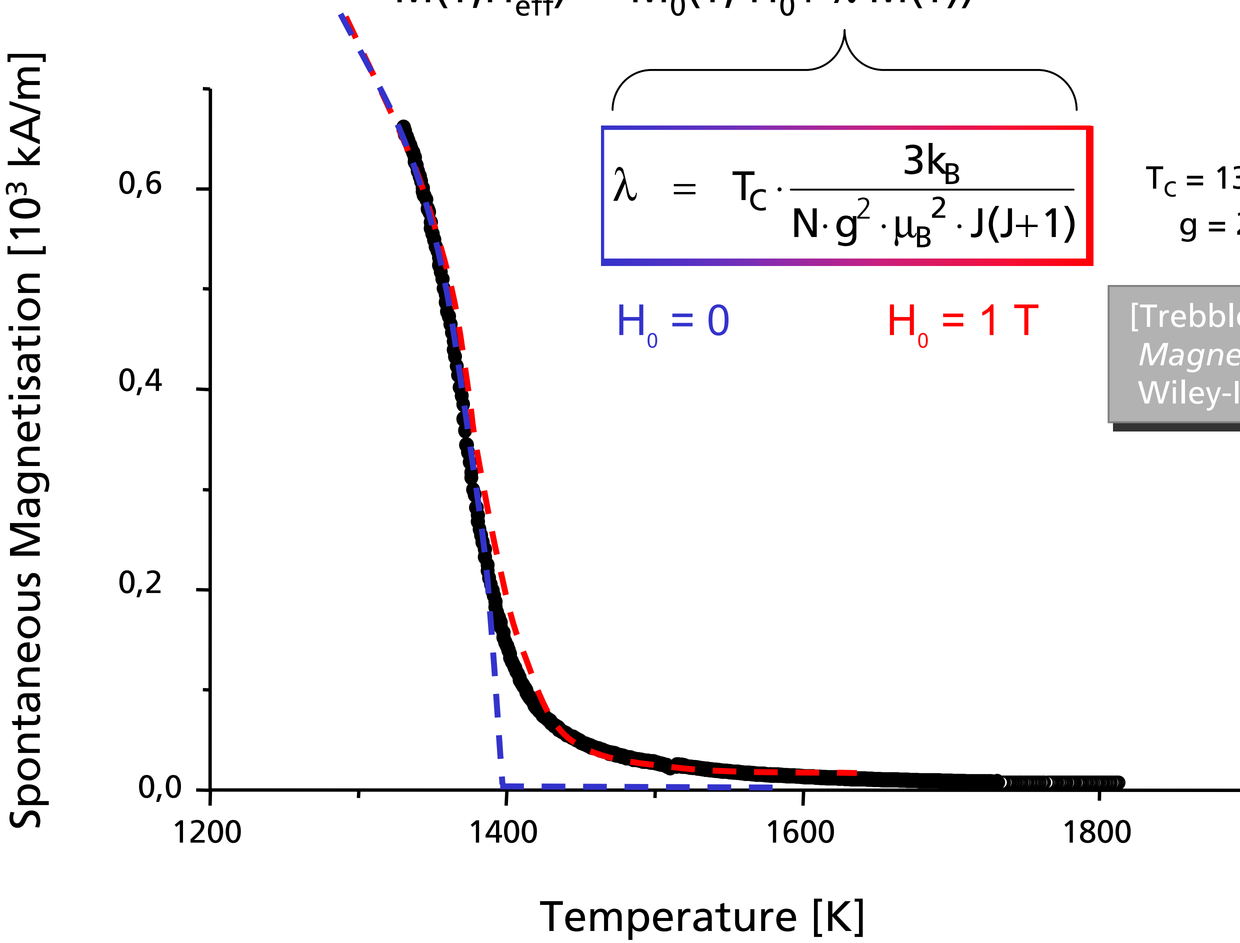
$$M(T,H_{eff}) = M_0(T, H_0 + \lambda\, M(T))$$

$$\lambda = T_C \cdot \frac{3k_B}{N \cdot g^2 \cdot \mu_B^2 \cdot J(J+1)}$$

T_C = 1394 K, J = S = ½,
g = 2.17, N = 1.61

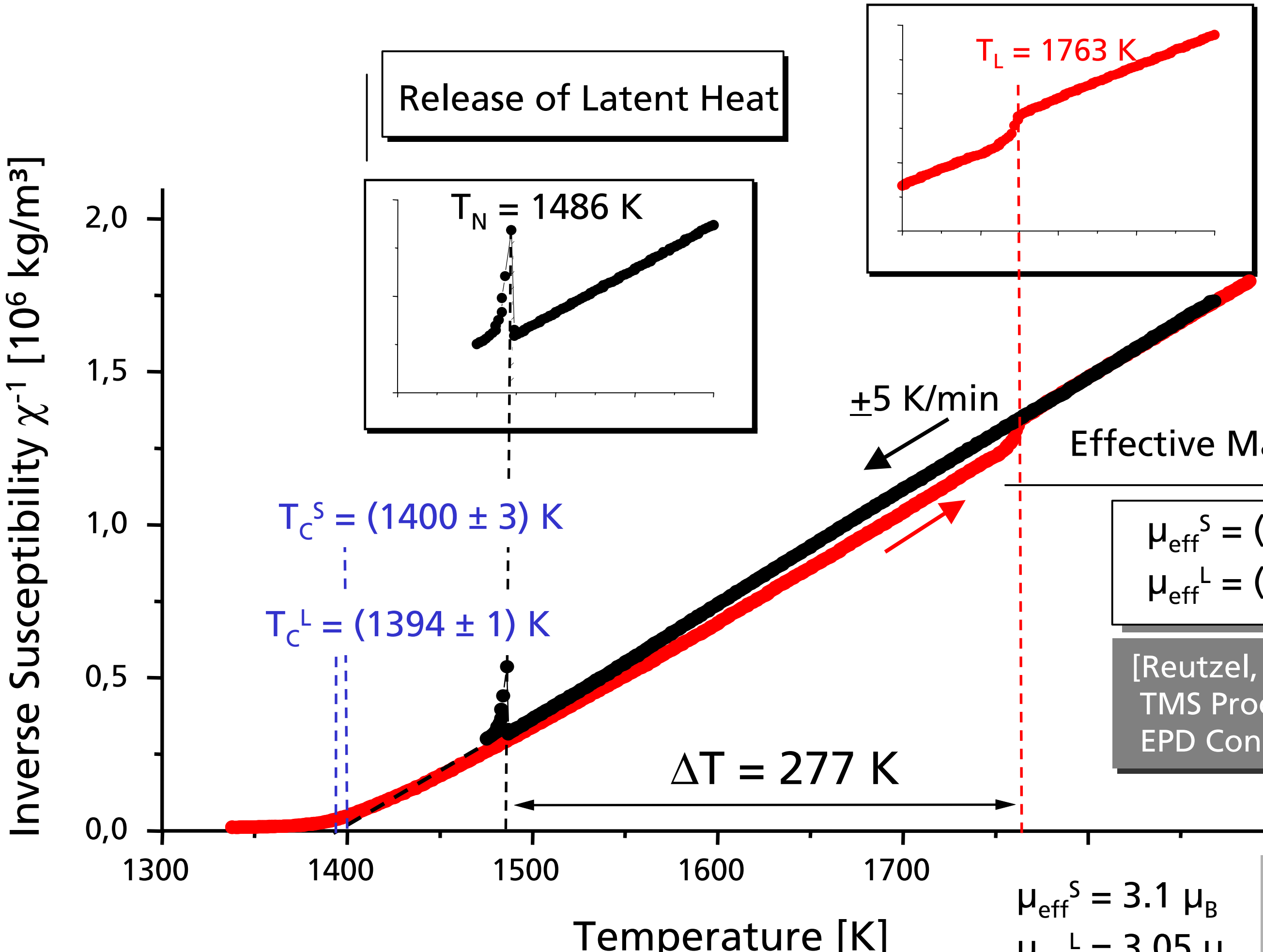
$H_0 = 0$ $H_0 = 1$ T

[Trebble, Craig, *Magnetic Materials*, Wiley-Interscience (1969)]



Inverse Susceptibility of **Cobalt**

$$\frac{1}{\chi} = \frac{3k_B}{N \cdot \mu_0 \cdot \mu_{eff}^2} \cdot T = \frac{1}{C} \cdot T$$



Effective Magnetic Moments

$\mu_{eff}^S = (3.18 \pm 0.06)\ \mu_B$

$\mu_{eff}^L = (3.15 \pm 0.06)\ \mu_B$

[Reutzel, Herlach, TMS Proceedings, EPD Congress, (2002), 609]

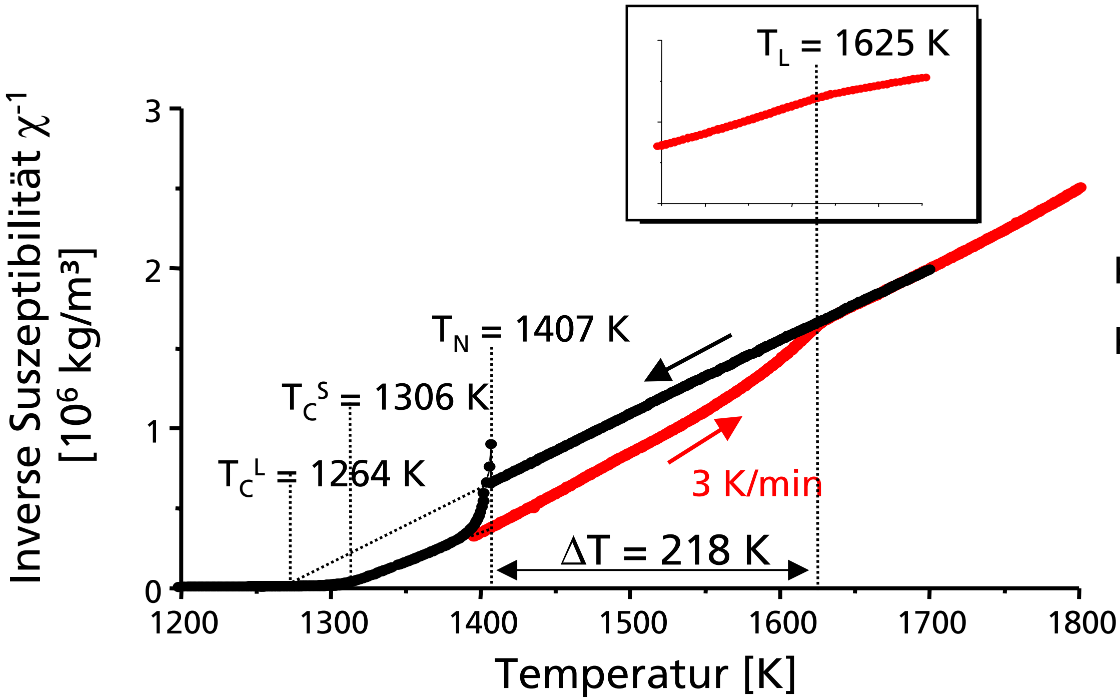
$\mu_{eff}^S = 3.1\ \mu_B$

$\mu_{eff}^L = 3.05\ \mu_B$

[Kamp, Methfessel, LAM 6 Proceedings, **1**, (1986), 575]

Completely Miscible Alloy System **Co-Pd**

Inverse Magnetic Susceptibility of $Co_{82}Pd_{18}$



$\mu_{eff}^{S} = (2.98 \pm 0.01)\ \mu_B$

$\mu_{eff}^{L} = (2.85 \pm 0.01)\ \mu_B$

$Co_{100-x}Pd_x$ Alloy Melts:

Increasing Co-Content

$\rightarrow$ Decrease of (T_C^S - T_C^L)

Co-Content [at.%]	82	100
T_C^S - T_C^L [K]	42	6

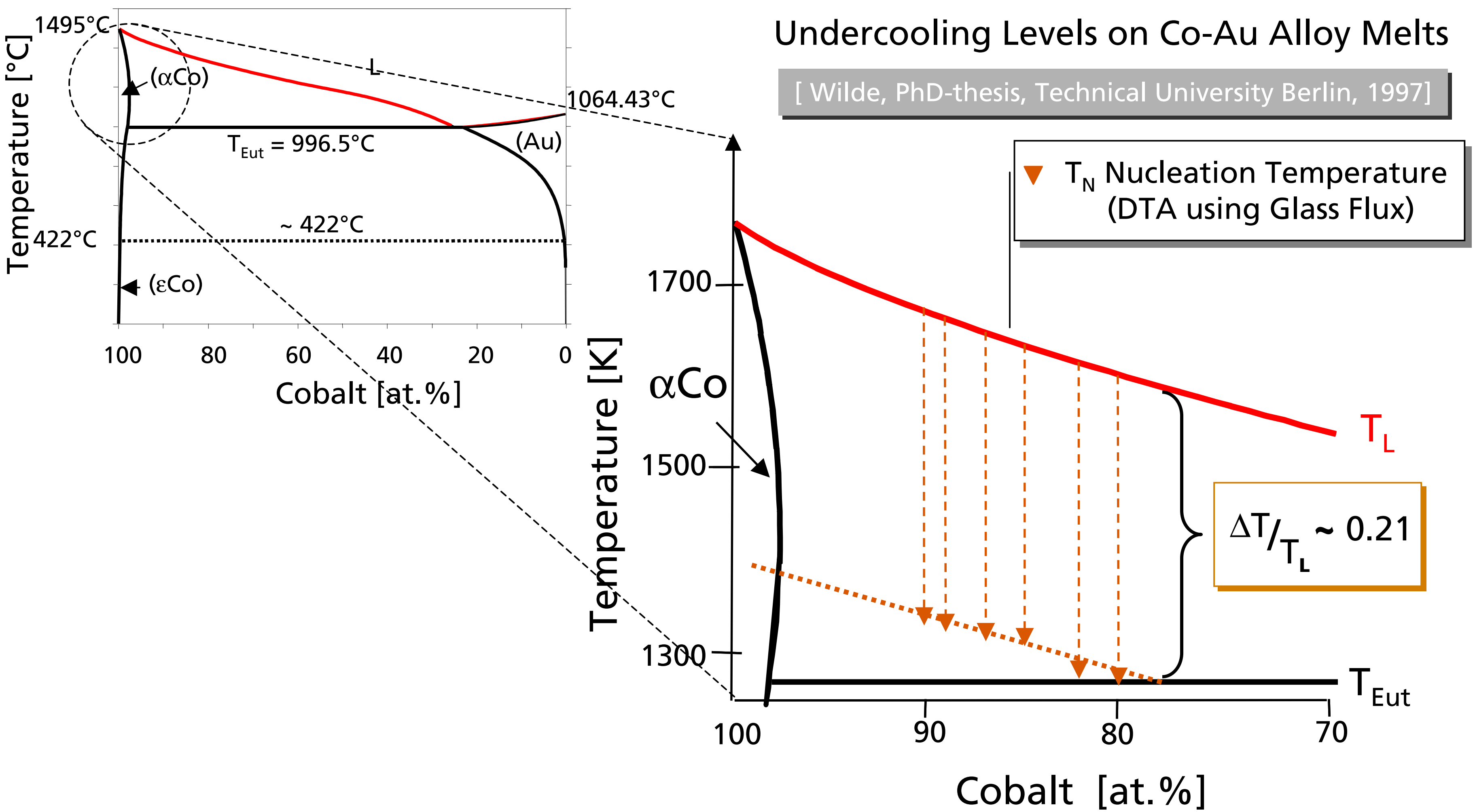
[Reutzel, PhD-thesis, Ruhr-University Bochum, 2002]

Eutectic Alloy System **Co-Au**

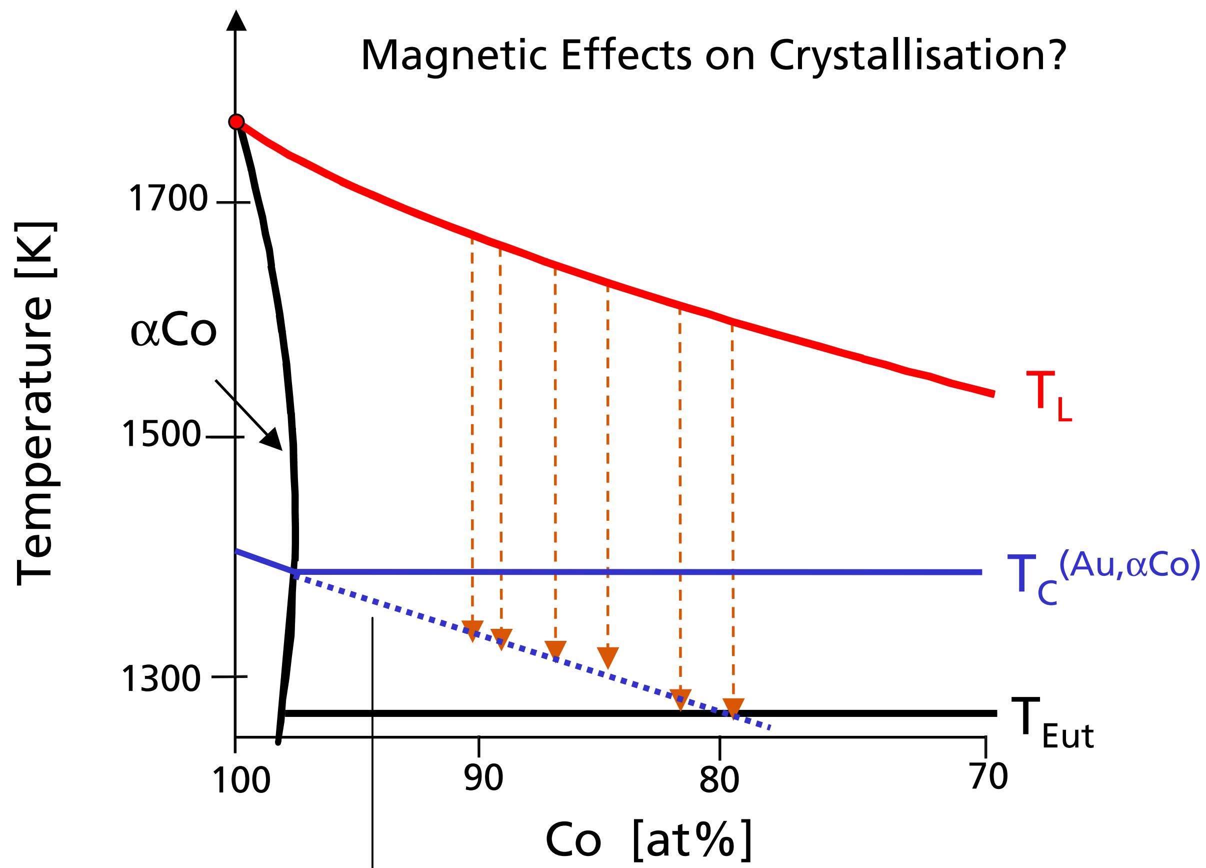
Equilibrium Phase Diagram

Undercooling Levels on Co-Au Alloy Melts

[Wilde, PhD-thesis, Technical University Berlin, 1997]



Eutectic Alloy System **Co-Au**

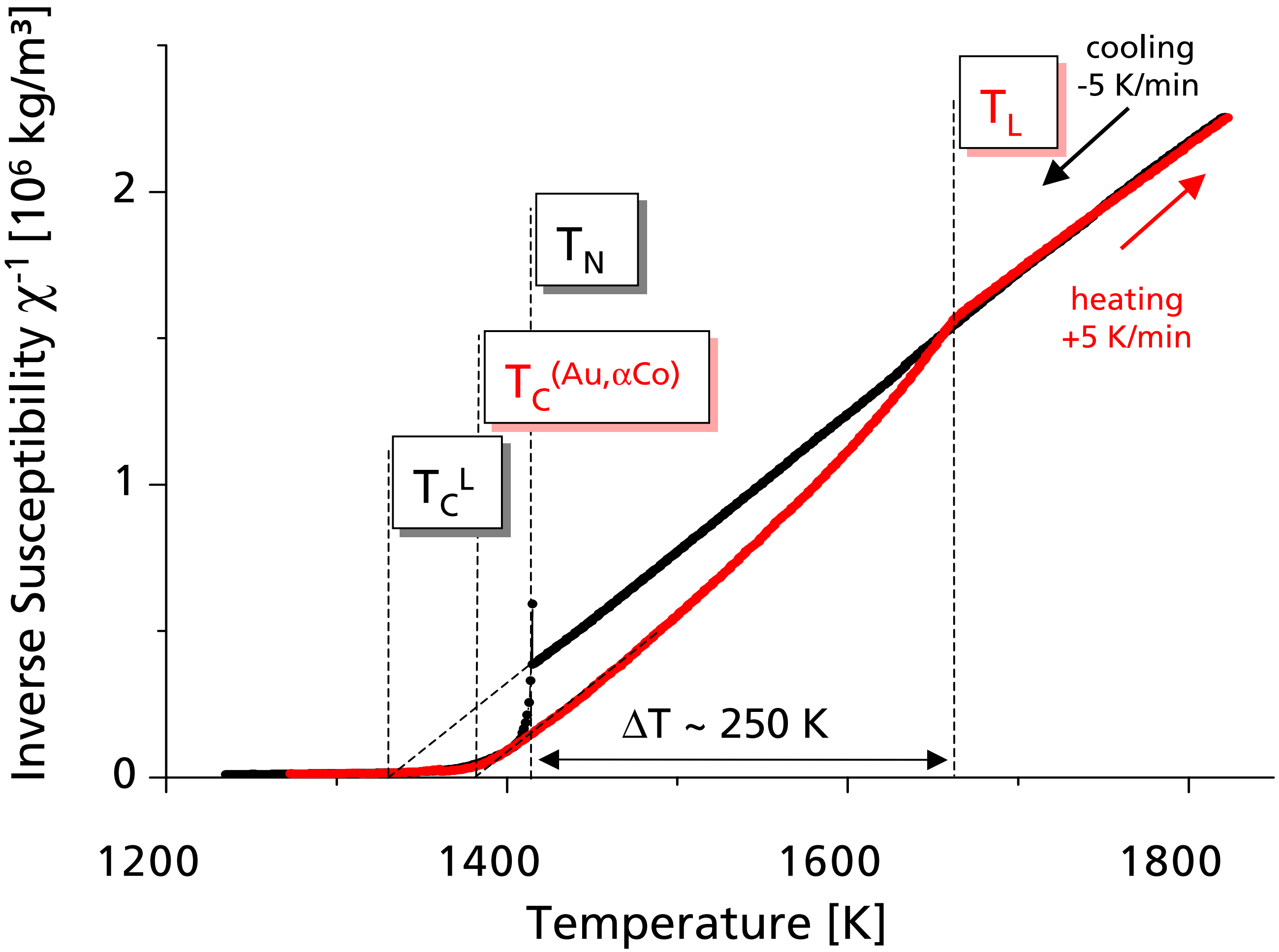


Assumption:

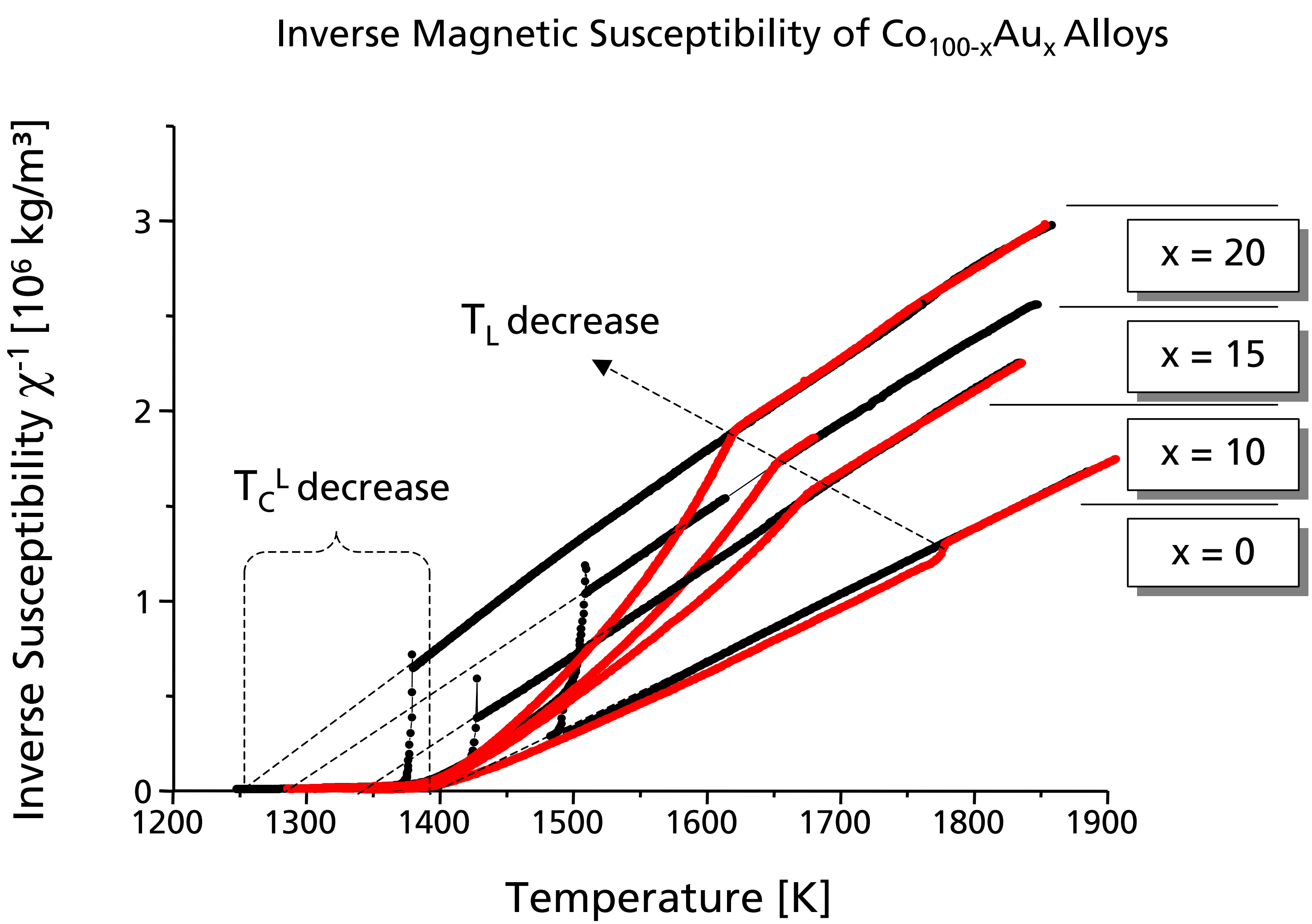
Curie-Temperature of Undercooled Liquid
Triggers Nucleation..?

Eutectic Alloy System **Co-Au**

Inverse Magnetic Susceptibility of $Co_{90}Au_{10}$

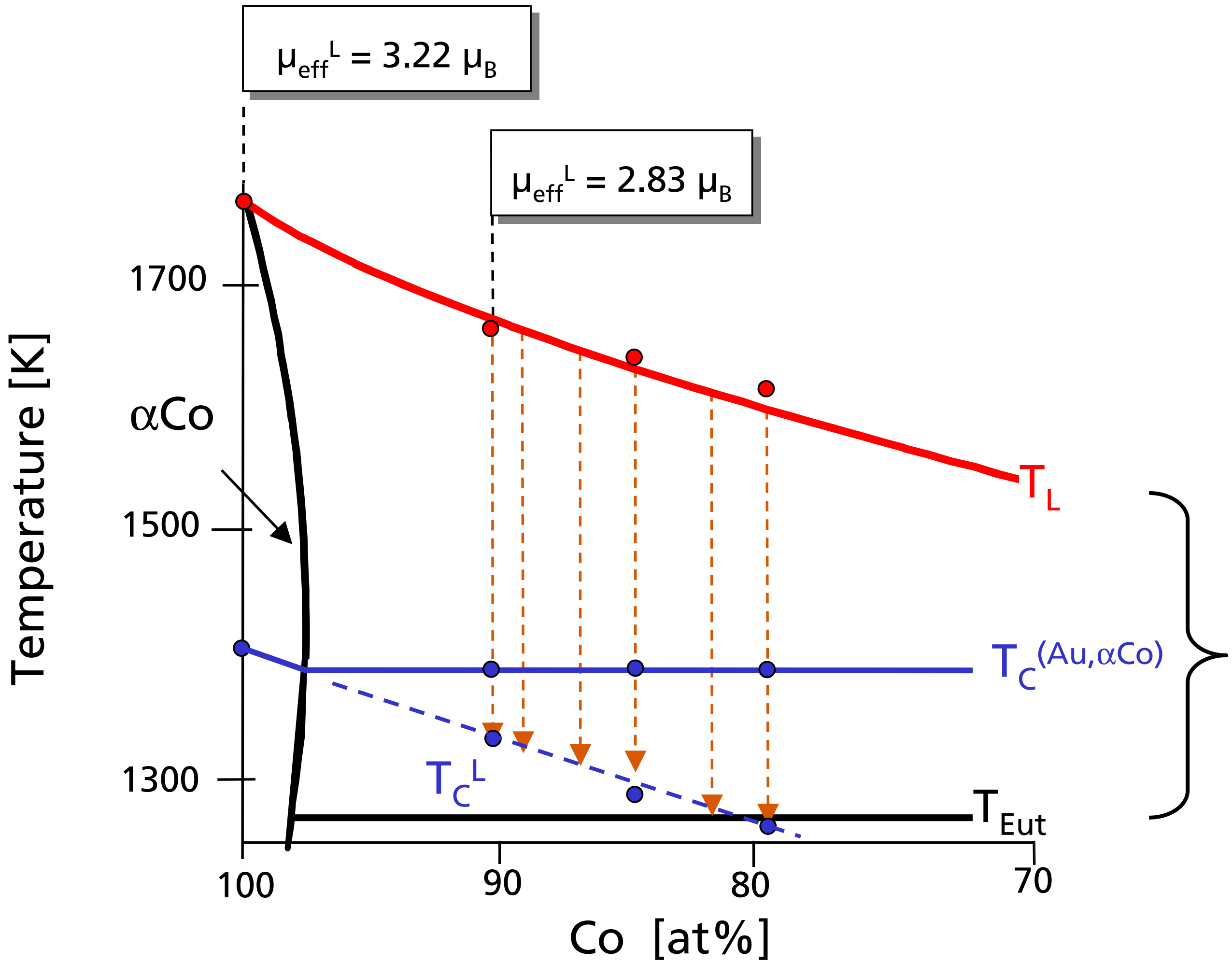


Eutectic Alloy System **Co-Au**



Magnetic Properties of Undercooled **Co-Au** Alloys

[Reutzel, Herlach, Mat. Sci. Eng. **A**, 375-377, (2004), 552]



$$\frac{T_L - T_C^L}{T_L} \sim 0.22$$

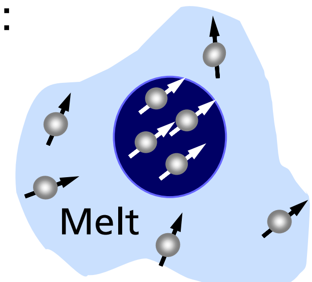
Résumé

Activation Energy

[Holland-Moritz, Spaepen
Phil. Mag. **84**, 10 (2004) 957]

$$\Delta G^* = \frac{16}{3}\pi \cdot \frac{(\sigma + \sigma_{mag})^3}{(\Delta G_V + \Delta G_{V,mag})^2}$$

Broken-Bond Model:



Ordered Cluster
(fcc)

(111)-Surface, $Z_{fcc} = 12$

3 Missing Nearest Neighbour Atoms!

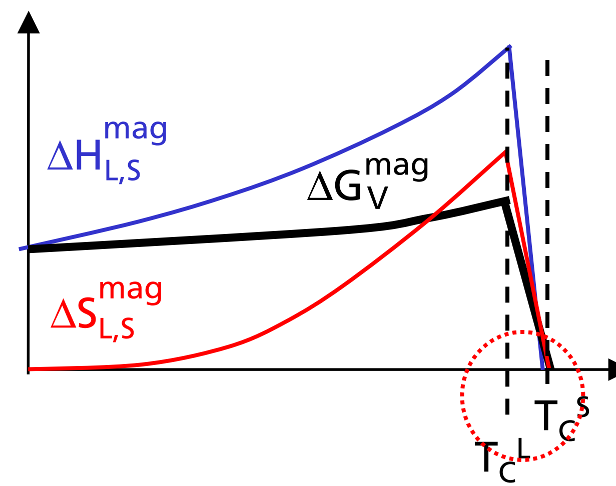
$$\Delta H_{mag}^{Surface} = -\frac{3}{12}\Delta H_{mag}^{Atom}$$

$$\sigma_{mag} = \sigma_{mag}(\Delta H_{mag}^{Atom})$$

$\sigma_{mag} \leq 1\%\ \sigma$

Molecular Field Theory:

$$\Delta G_V^{mag} = \Delta H_{L,S}^{mag} - T\Delta S_{L,S}^{mag}$$



$\Delta G_V^{mag} \leq 15\%\ \Delta G_V(T_N)$

ΔG^* Lowered by Magnetic Contribution!

Résumé

I Precise Detection of Magnetic Properties of Undercooled **Co** and **Co-Pd-** & **Co-Au-**Alloy Melt at Elevated Temperatures!

II Detected Curie-Temperatures of Liquid Phase of Cobalt and of Co-Pd- & Co-Au-Alloy Systems Correspond to Maximum Undercooling Levels

III Crystal Nucleation in Undercooled Liquid Affected by Onset of Magnetic Ordering

IV Formulation of Extended Nucleation Model Useful to Describe Limited Experimental Undercooling Levels

Contributors

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T. Volkmann

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