Thermodynamic assessments of systems evaluated in the WenDeLIB priority programme for Li-ion batteries

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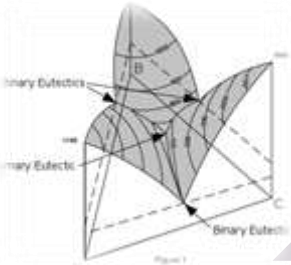
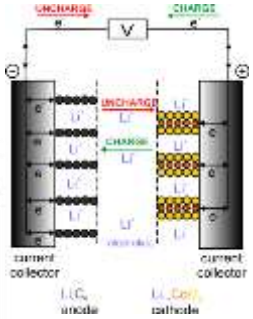
INSTITUTE FOR APPLIED MATERIALS – APPLIED MATERIALS PHYSICS (IAM-AWP)

Why WenDeLIB





Active Material

Constitution

Cell

Battery

Integration

Application

Materials Thermodynamics and Kinetics

Heterogeneous Equilibria

Preparation and Synthesis

Electrochemical Investigations

Priority Program 1473

SPP 1473: Materials with New Design for Improved Lithium Ion Batteries – WeNDeLIB

Joint Project 12: Thermodynamics and kinetics for stabilization of conversion type electrodes for LIB based on nano 3d transition metal oxide composites

- Modification of nano 3d transition metal oxide composites and their influence on thermodynamics and kinetics (Dr. Gruner, Dr. Ehrenberg – IFW Dresden)
- Thermodynamic description of stabilization of nano-materials (Prof. Seifert – KIT)
- Microstructure features behind the degredation of nanocrystalline 3d transition metal oxide composites (Prof. Rafaja – TU BA Freiberg)
- Influence of electrolyte on stabilization of 3d transition metal oxide composites (Prof. Winter, Dr. Trill – WWU Münster)

Motivation

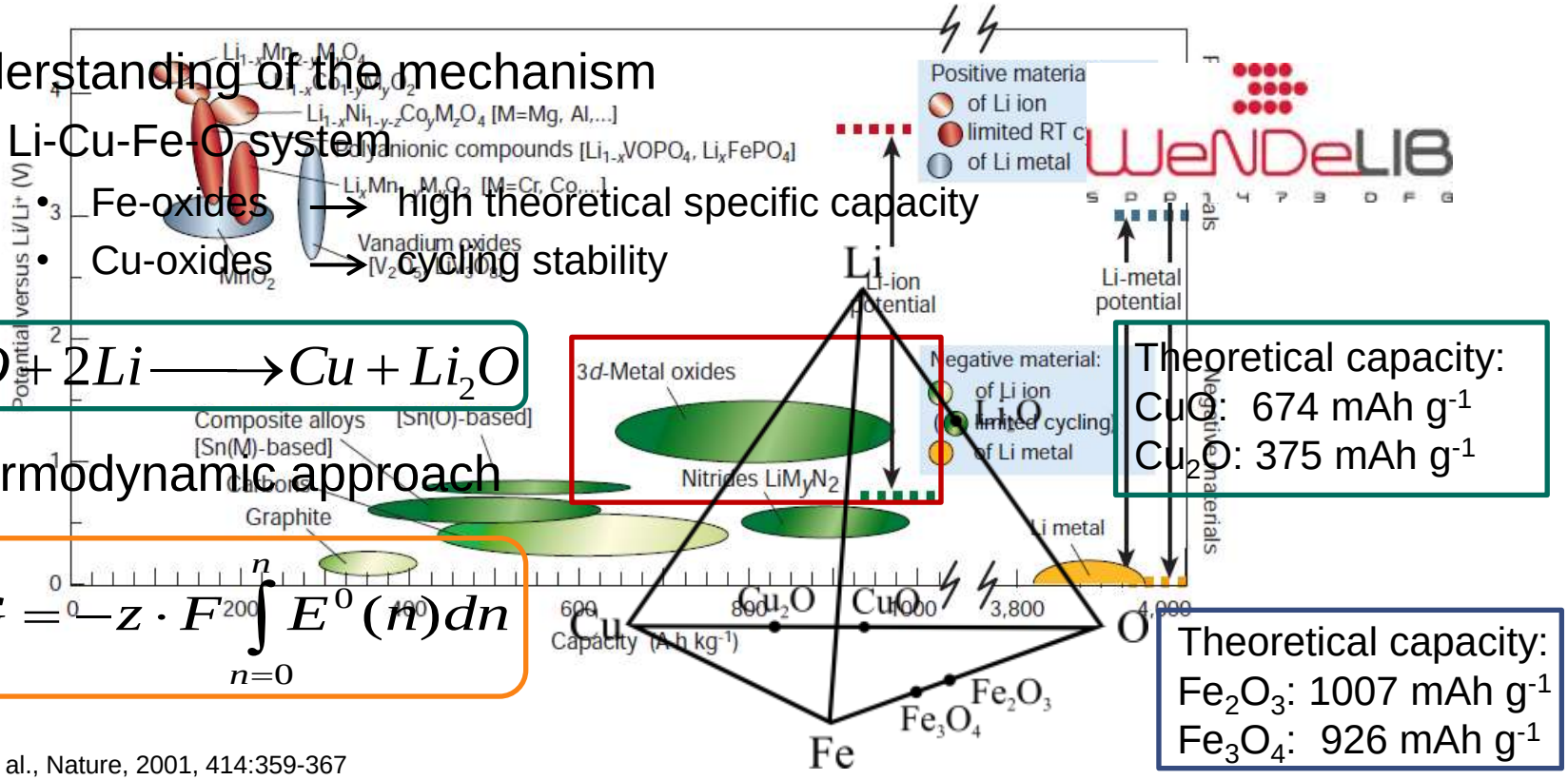
- 3d transition metal oxides
  - Conversion mechanism
  - High theoretical specific capacity

- Understanding of the mechanism
  - Li-Cu-Fe-O system
    - Fe-oxides → high theoretical specific capacity
    - Cu-oxides → cycling stability

- Thermodynamic approach

$$CuO + 2Li \longrightarrow Cu + Li_2O$$

$$\Delta G = -z \cdot F \int_{n=0}^{n} E^0(n)\,dn$$



Theoretical capacity:
CuO: 674 mAh g^{-1}
Cu_2O: 375 mAh g^{-1}

Theoretical capacity:
Fe_2O_3: 1007 mAh g^{-1}
Fe_3O_4: 926 mAh g^{-1}

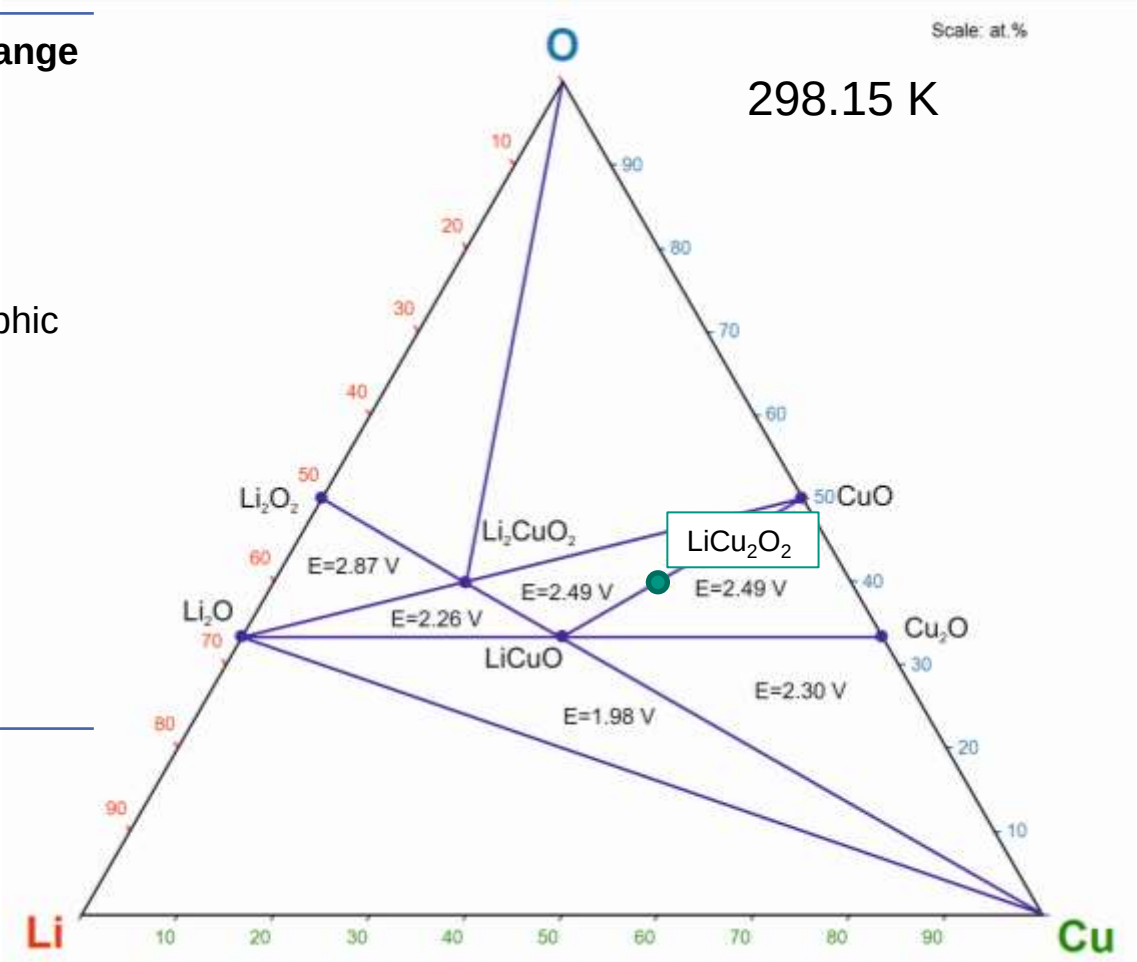
J.M. Tarascon et al., Nature, 2001, 414:359-367

Literature Data in the Li-Cu-O System

Phase	Temperature stability range
LiCuO	< 980 °C
Li_2CuO_2	< 1020 °C
$LiCu_2O_2$	890 – 1050 °C in air
	stable in argon, polymorphic
	transition around 720 °C
$LiCu_3O_3$	> 800 °C in air
$LiCuO_2$**	
Li_3CuO_3	
$Li_3Cu_2O_4$	250 – 330 °C in oxygen

**can be only synthesized via delithiation of Li_2CuO_2

Is the $LiCu_2O_2$ phase stable?



N.A. Godshall, Solid State Ionics 1986, 18&19:788-793

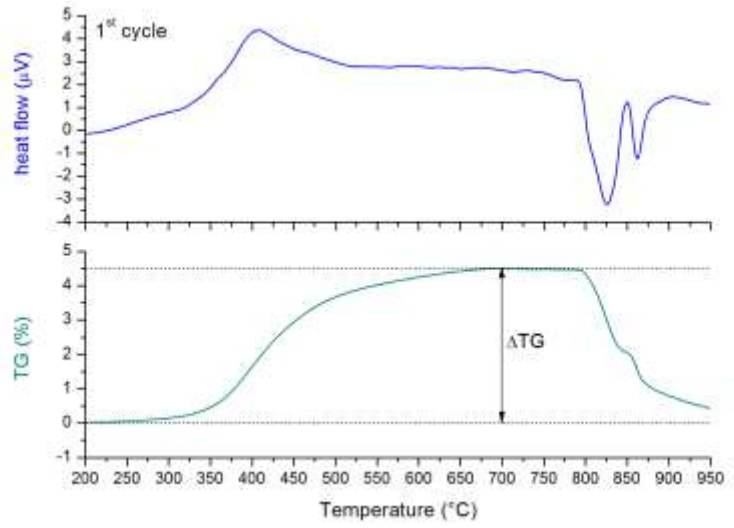
S. Patat et al., Solid State Ionics 1991, 46:325-329

Phase Stability of $LiCu_2O_2$

- Sample synthesis via mixed oxide method from CuO, Cu_2O and Li_2CO_3
- In argon / 20 % oxygen mixture
- Simultaneous DTA/TG (Setaram)
- 200-950°C, HR=10 K/min, 3 cycles

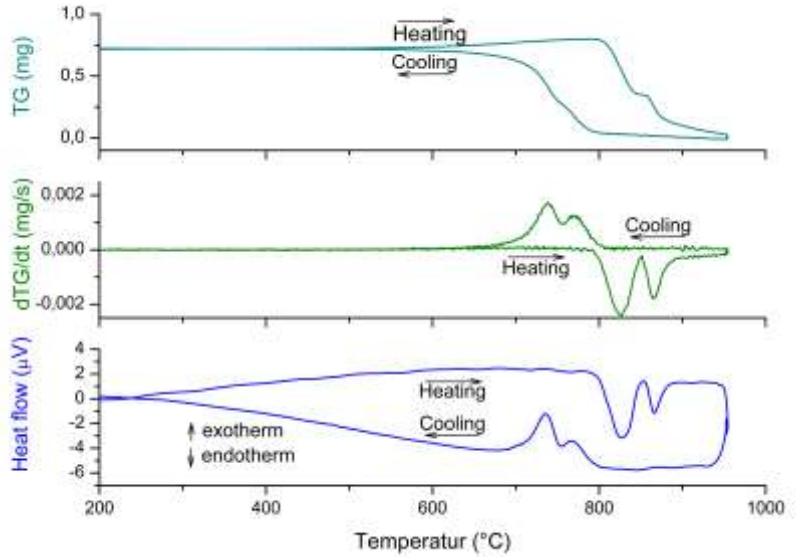
- Irreversible phase transformation accompanied with mass gain ΔTG during 1st cycle

$$2LiCu_2O_2 + \frac{1}{2}O_2 \rightarrow Li_2CuO_2 + 3CuO$$



- Reversible step reaction in 2nd and 3rd cycles
  - Formation of $LiCu_3O_3$ and $LiCu_2O_2$ (in accordance to Bush et al.)

A.A. Bush et al., Inorganic Materials, 2004, 40:44-49

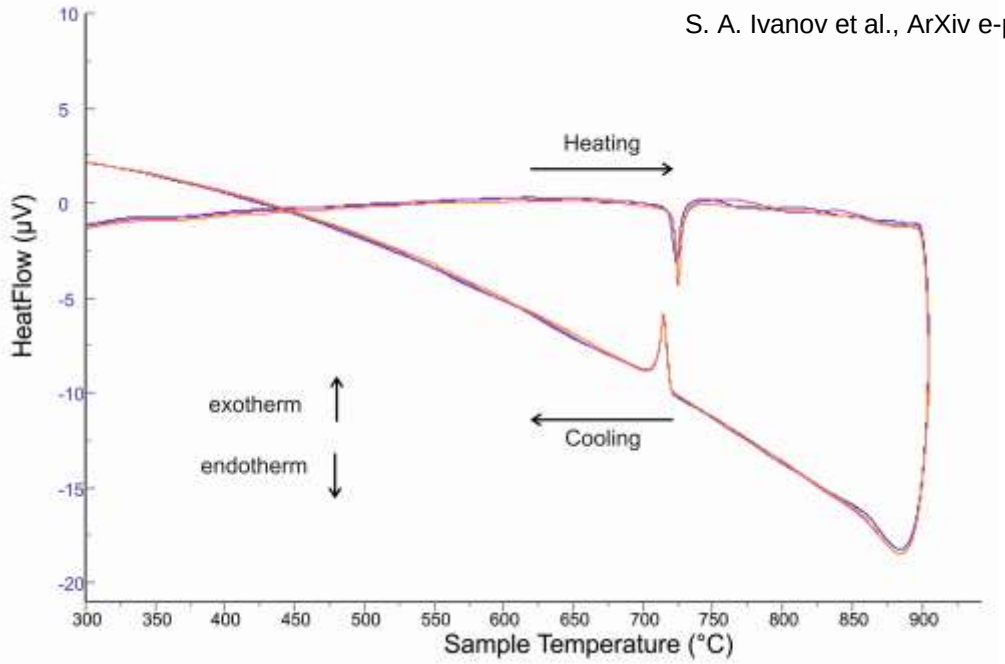


Phase Stability of $LiCu_2O_2$

- Sample synthesis via mixed oxide method from CuO Cu_2O, Li_2CO_3
- In argon
- Simultaneous DTA/TG (Setaram)
- 200-900°C, HR=10 K/min, 3 cycles

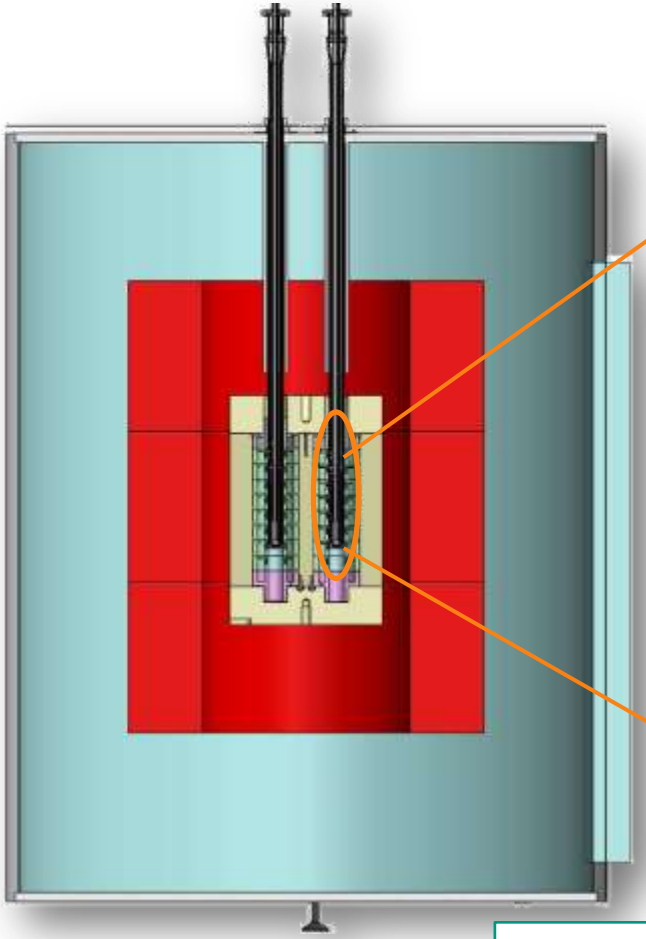
- Reversible phase transformation at 720 °C
  - First order transformation from orthorhombic to tetragonal $LiCu_2O_2$ (according to Ivanov et al.)

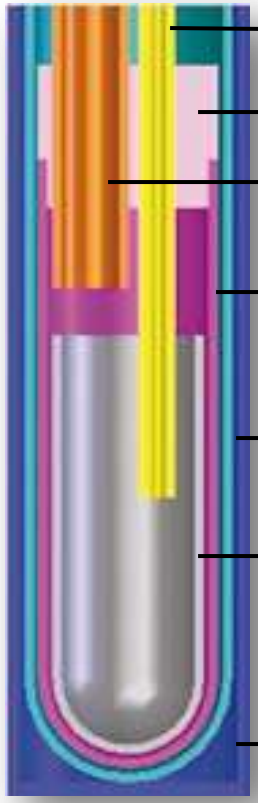
S. A. Ivanov et al., ArXiv e-prints, Nov. 2012



$LiCu_2O_2$ is stable at low oxygen partial pressures

Enthalpy of Formation: Drop Solution Calorimetry





Platinum tube for bubbling gas

Al_2O_3 lid

SiO_2 glass dropping tube

SiO_2 crucible, 28 ml volume

SiO_2 glass liner

Platinum crucible, 20 ml volume

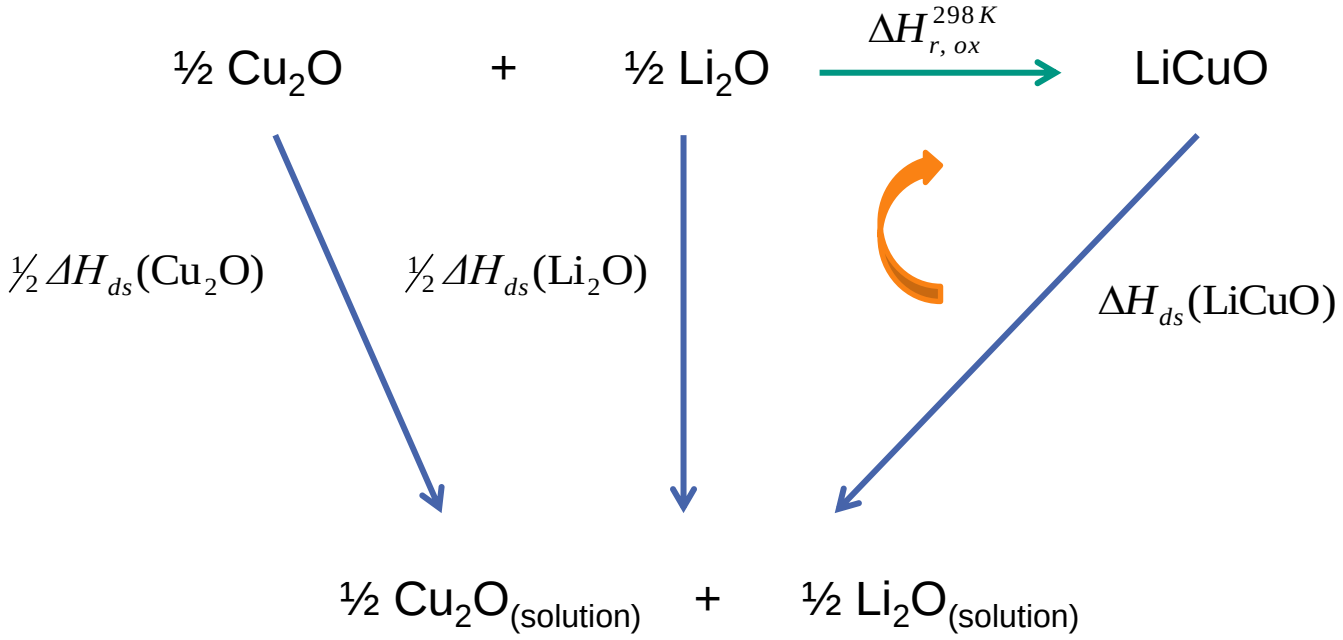
Inconel protection tube

- Twin Calvet type calorimeter
- Sensitivity: 0.00463828 J/µVs (Left Side), 0.00466871 J/µVs (Right Side)
- Sodium molybdate ($3Na_2O{\cdot}4MoO_3$) solvent used for solution calorimetry
- Solution calorimetry performed at 700°C

Solution Calorimetry

- Determination of enthalpies of formation of the ternary compounds in the Li-Cu-O system

1. Thermodynamic cycle: enthalpy of formation from the oxides



$$\Delta H_{r,\,ox}^{298K} = \tfrac{1}{2}\Delta H_{ds}(Cu_2O) + \tfrac{1}{2}\Delta H_{ds}(Li_2O) - \Delta H_{ds}(LiCuO)$$

Solution Calorimetry

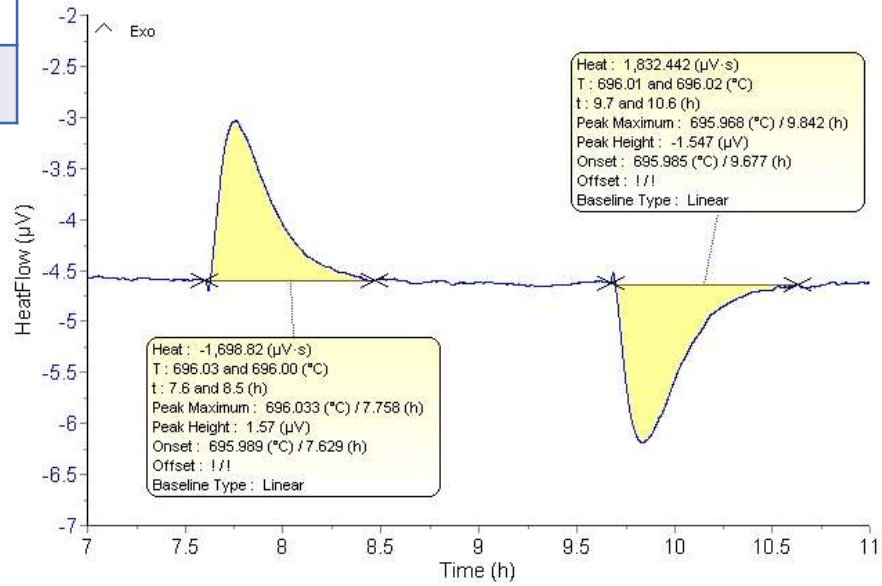
- Determination of enthalpies of formation of the ternary compounds in the Li-Cu-O system

2. Determination of enthalpies of solution of
   - Binary oxides

	Navrotsky	This work
Li_2O	-93 ± 2.3 kJ/mol**	-
CuO	44.2 ± 0.4 kJ/mol*	44 ± 1 kJ/mol
Cu_2O	-	-67 ± 1.5 kJ/mol

   - Ternary oxides LiCuO, …

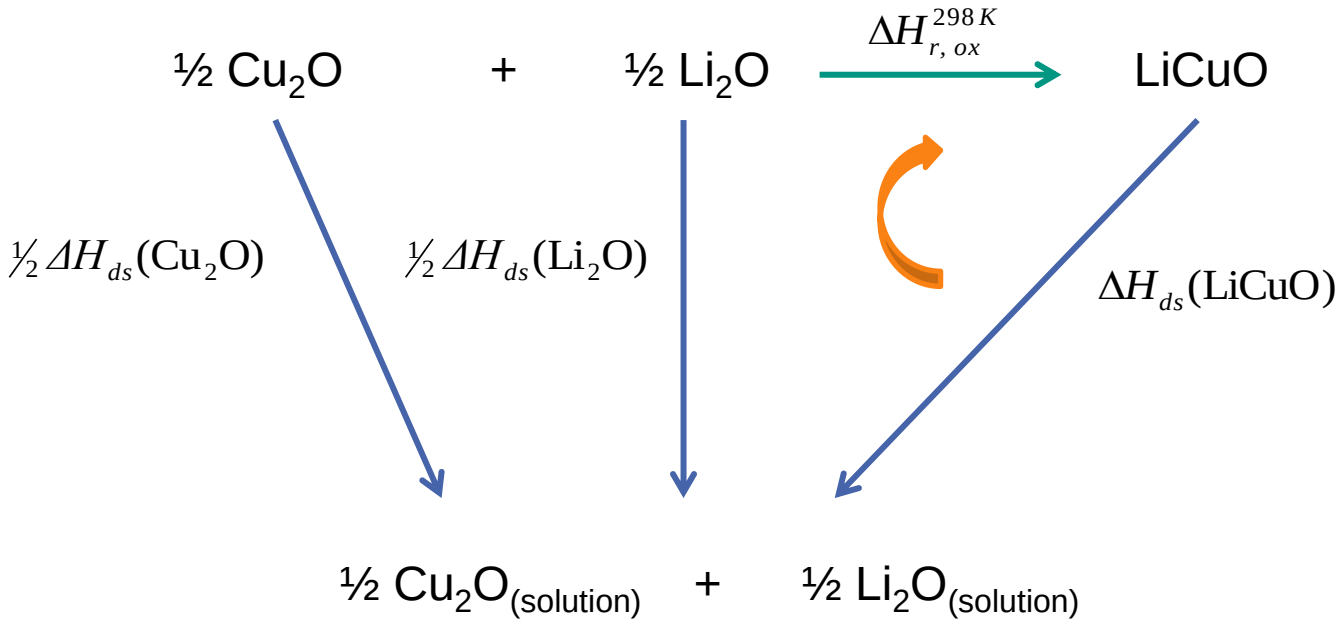
	This work
LiCuO	-69 ± 1 kJ/mol



*M. Wang, A. Navrotsky, Solid State Ion. 166 (2004)
**S-N. Le, A. Navrotsky, V. Pralong, Solid State Sciences 10 (2008)

Solution Calorimetry

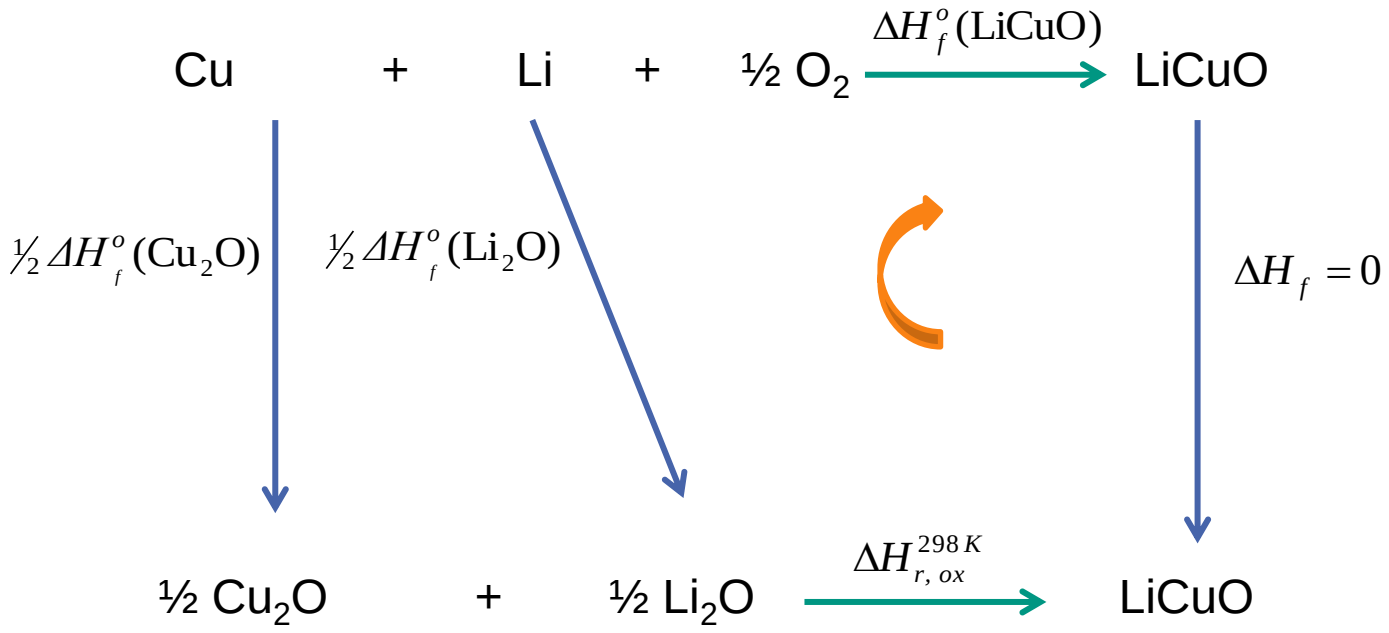
Thermodynamic cycle: enthalpy of formation from the oxides



$$\Delta H_{r,\,ox}^{298K} = \tfrac{1}{2}\Delta H_{ds}(Cu_2O) + \tfrac{1}{2}\Delta H_{ds}(Li_2O) - \Delta H_{ds}(LiCuO) = -11\,^{kJ}/_{mol}$$

Solution Calorimetry

Thermodynamic cycle: enthalpy of formation from the elements



$$\Delta H_f^0(\mathrm{LiCuO}) = \tfrac{1}{2}\Delta H_f^o(\mathrm{Cu_2O}) + \tfrac{1}{2}\Delta H_f^o(\mathrm{Li_2O}) + \Delta H_{r.ox}(\mathrm{LiCuO}) = -394 \pm 4\ ^{kJ}/_{mol}$$

	Patat et al.	This work
LiCuO	-390 ± 1 kJ/mol	-394 ± 4 kJ/mol

S. Patat et al., Solid State Ionics 1991, 46:325-329

Thermodynamic Modeling of the Li-Cu-O System

- Description via the reaction from the binary oxides

$$m\mathrm{Li_2O} + n\mathrm{Cu_2O} + p\mathrm{CuO} \leftrightarrow \mathrm{Li_{2m}Cu_{2n+p}O_{m+n+p}}$$

- Gibbs energy of reaction at 25 °C

Patat et al.

$$\Delta_r G_{\mathrm{Li_{2m}Cu_{2n+p}O_{m+n+p}}} = \Delta_r H_{\mathrm{Li_{2m}Cu_{2n+p}O_{m+n+p}}} - T\Delta_r S_{\mathrm{Li_{2m}Cu_{2n+p}O_{m+n+p}}}$$

$$= \Delta_f G^o_{\mathrm{Li_{2m}Cu_{2n+p}O_{m+n+p}}} - m\Delta_f G^o_{\mathrm{Li_2O}} - n\Delta_f G^o_{\mathrm{Cu_2O}} - p\Delta_f G^o_{\mathrm{CuO}}$$

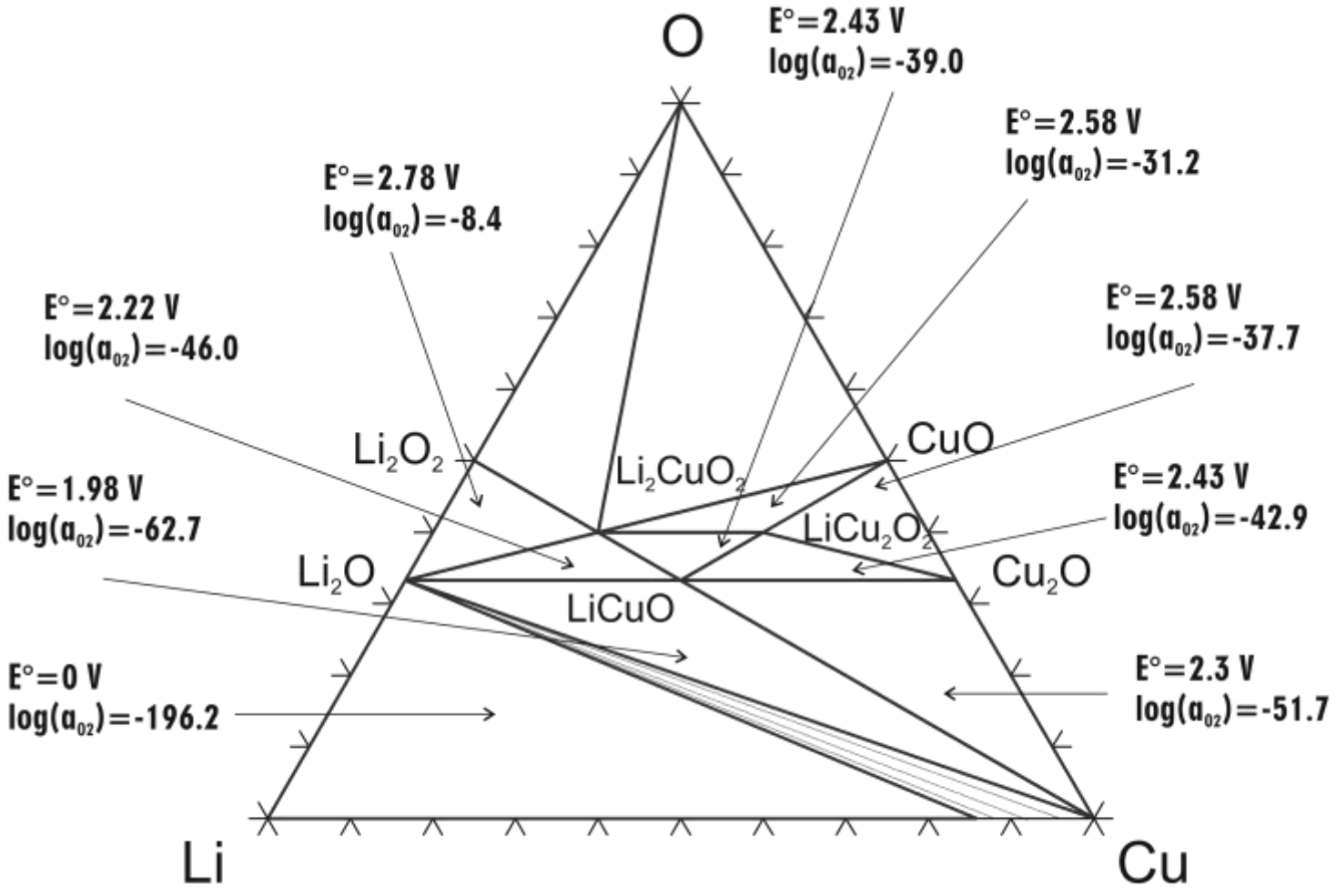
Godshall

Binary descriptions

- Simplified model for description of the ternary phases
- Good description for the battery relevant temperature regime

N.A. Godshall, Solid State Ionics 1986, 18&19:788-793 S. Patat et al., Solid State Ionics 1991, 46:325-329

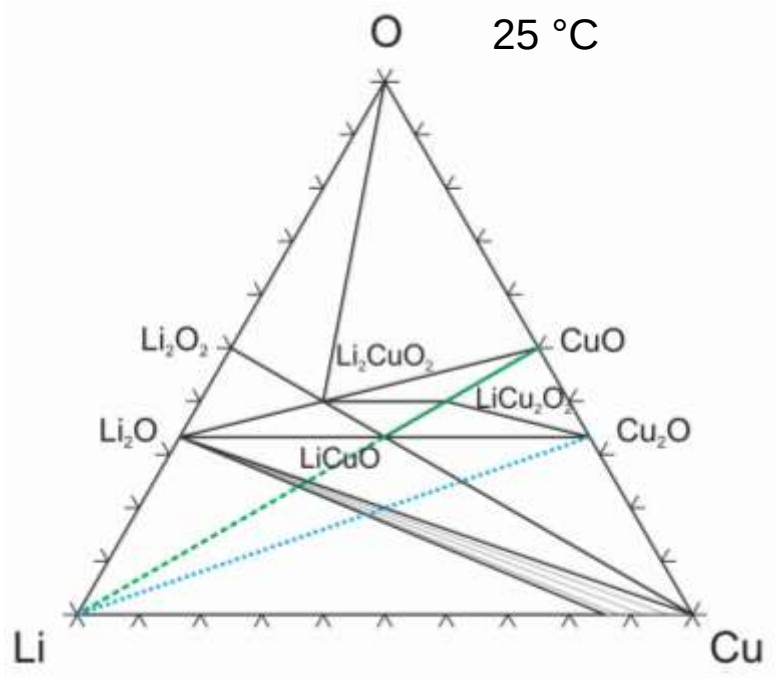
Calculated Li-Cu-O System at 25 °C

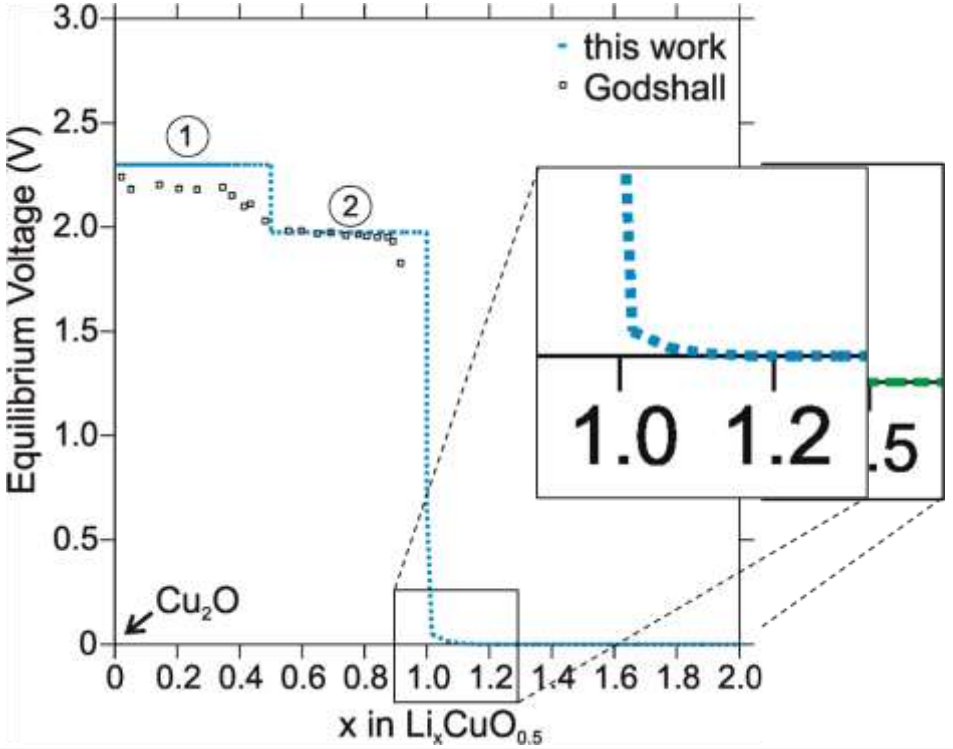


Calculated Titration Curves

- Equilibrium cell voltage as a function of lithium content at the cathode along selected composition paths

$$E = -\frac{\mu_{Lithium}^{cathode}}{z \cdot F}$$





Experimental Thermodynamics and Phase Relations of New Electrode Materials for Li-Ion-Batteries

universität wien

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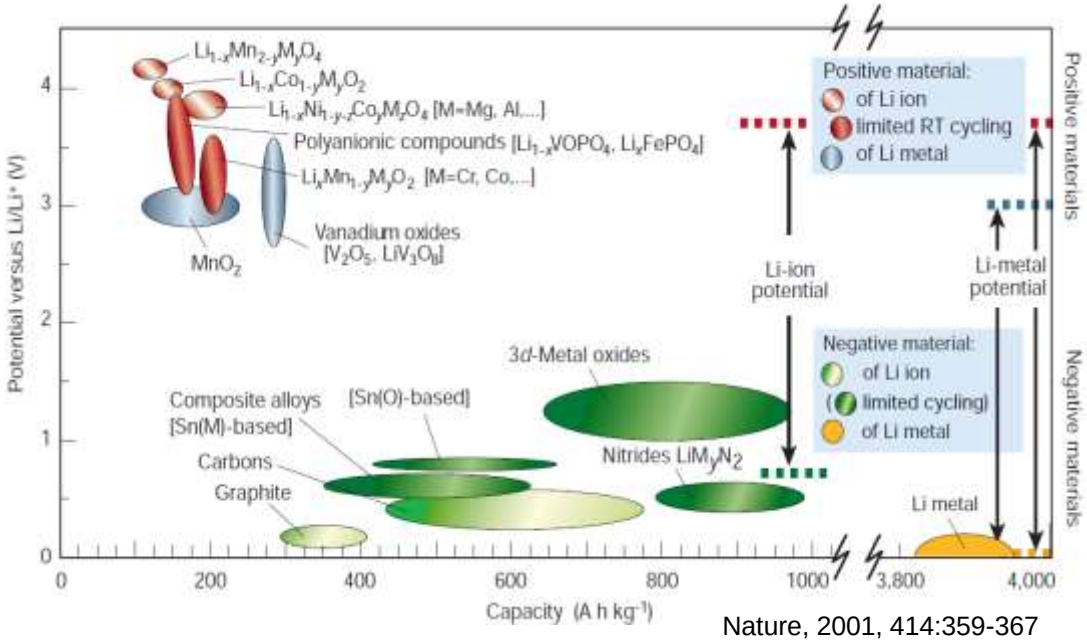
Torsten Markus
David Henriques

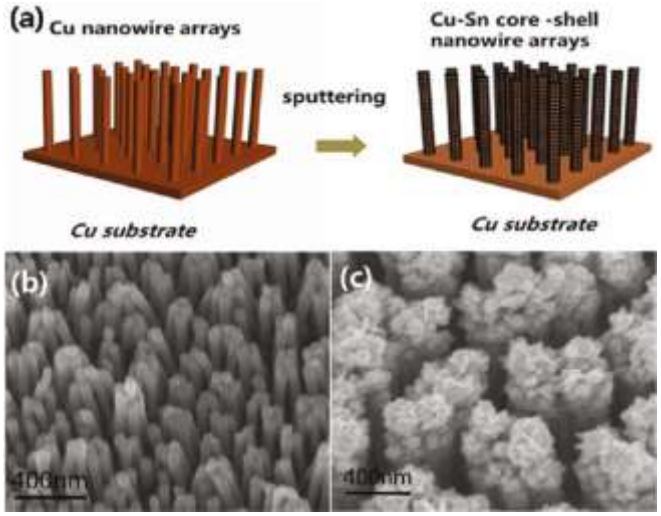
JÜLICH FORSCHUNGSZENTRUM

Studies in the systems Li-Sn, Cu-Li, Cu-Li-Sn and Li-Mn-O

Why Cu-Li-Sn?



Nature, 2001, 414:359-367

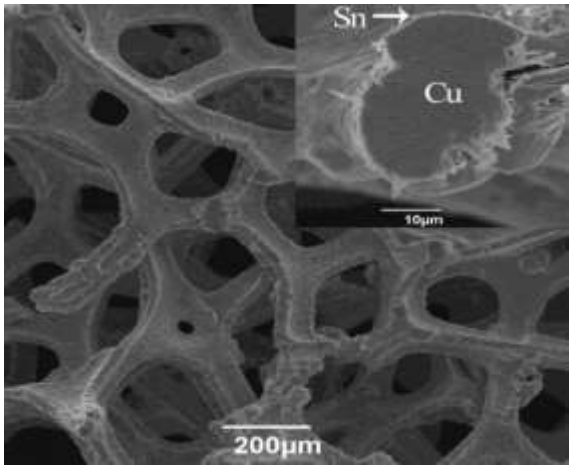


J. Phys. Chem. C 2011, 115, 23620–23624

Metal alloy anodes (e.g. Sn based):

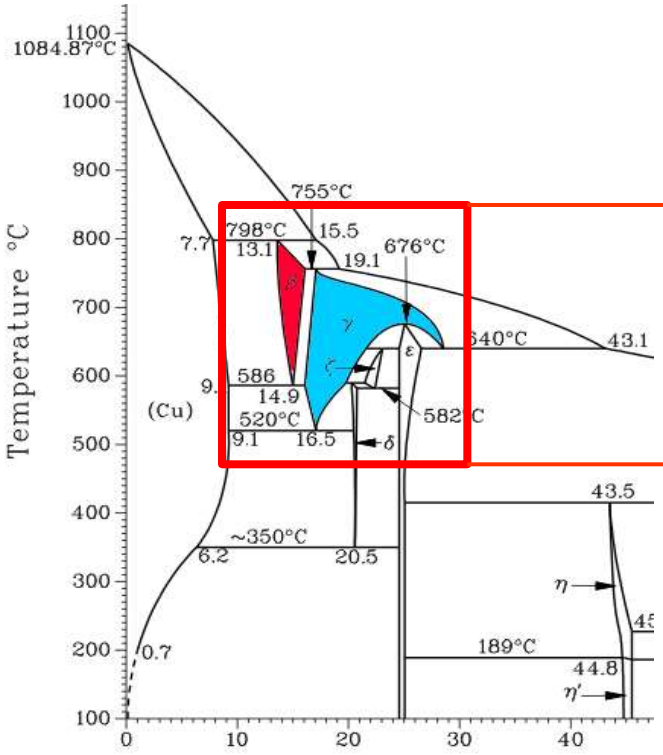
- ✓ High charge density (992mAh/g for $Li_{4.4}Sn$)
- ✓ High potential
- ✘ Volume changes during intercalation / deintercalation leads to electrode degradation
- ✓ Cu matrix can buffer the volume changes Li-Sn

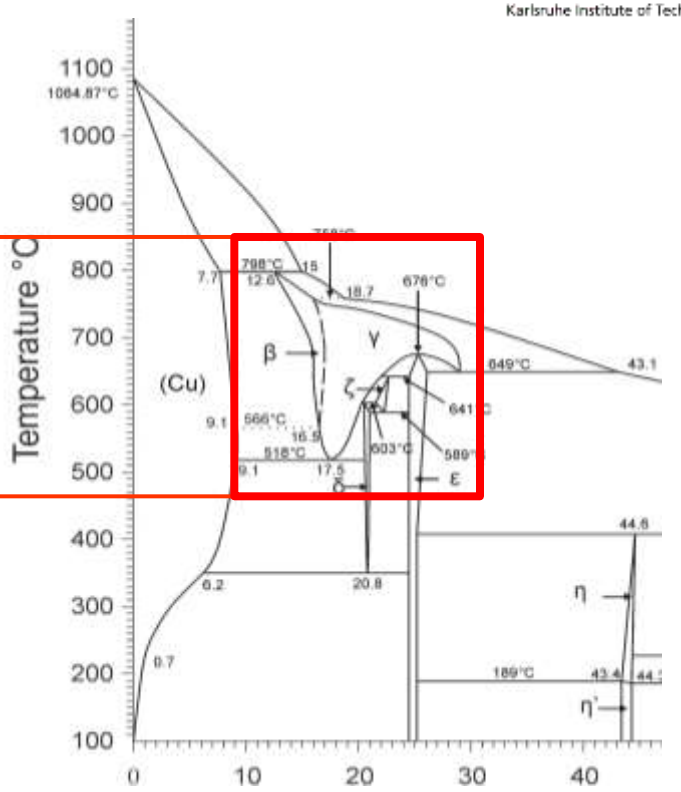
- No Cu-Li-Sn ternary phase diagram avaliable
- (Cu,Li)-Sn binary phase diagrams need to be revised



Adv. Mater. 2010, 22, 5154–5158

Cu-Sn

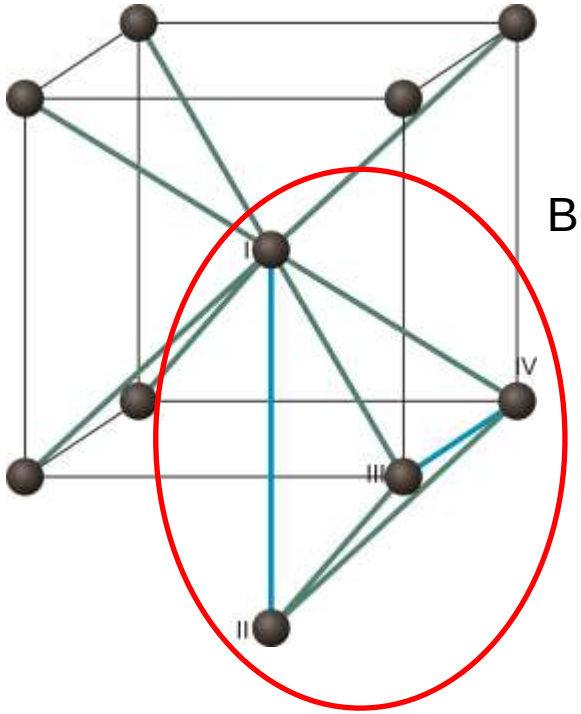




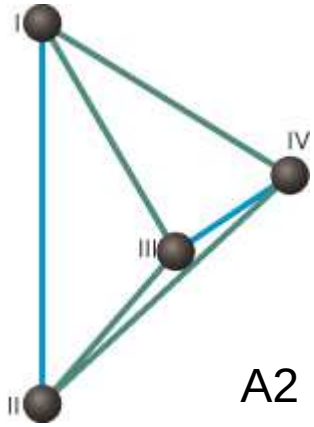
T.B. Massalski, H. Okamoto, Binary alloy phase diagrams, ASM International, Materials Park, Ohio, 2001.

S. Fürtauer, D. Li, D. Cupid, H. Flandorfer, Intermetallics 34 (2013) 142-147.
D. Li, P. Franke, S. Fürtauer, D. Cupid, H. Flandorfer, Intermetallics 34 (2013) 148-158.

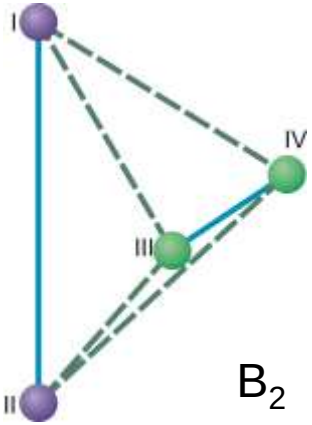
Modeling: Ground States of the BCC Structure



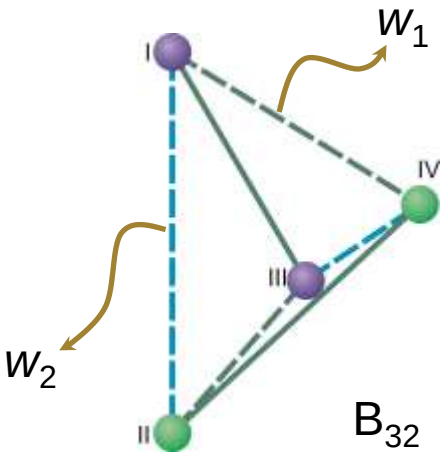
BCC



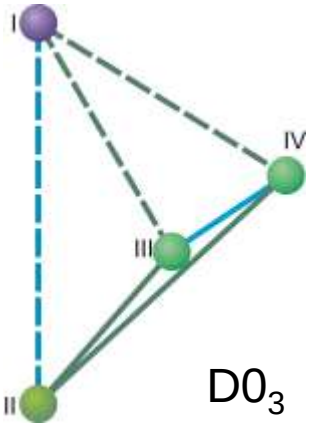
A2



B_2



B_{32}



$D0_3$

A2/$D0_3$ model: $(Cu,Sn)^{I}_{0.25}(Cu,Sn)^{II}_{0.25}(Cu,Sn)^{III}_{0.25}(Cu,Sn)^{IV}_{0.25}$

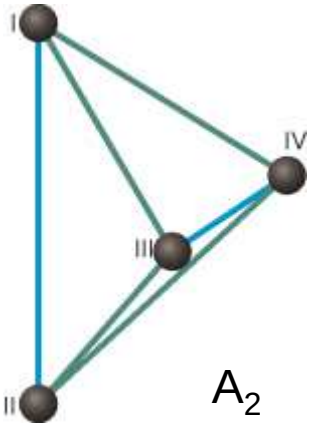
Ordering Model

$$G_m = G_m^{dis}\left(x_i\right) + G_m^{ord}\left(y_i^{(s)}\right) - G_m^{ord}\left(x_i\right)$$

Ansara, I. et al., Calphad, 1997. 21(4): 535-542.

$$G_m^{ord}(y_i^{(s)}) = \sum_i \sum_j \sum_k \sum_l y_i^I y_j^{II} y_k^{III} y_l^{IV} G_{i:j:k:l}^{4SL} + 0.25RT \sum_i \sum_S y_i^{(s)} \ln y_i^{(s)}$$

Sundman, B., and J. Agren, 1981, J. Phys. Chem. Solids, 42: 297-301.



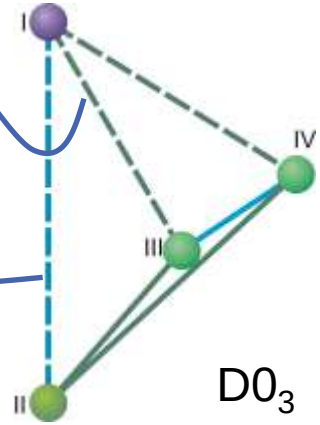
A_2

B2: $G_{Cu:Cu:Sn:Sn}^{4SL} = G_{Sn:Sn:Cu:Cu}^{4SL} = -4w_1$

B32: $G_{Cu:Sn:Cu:Sn}^{4SL} = G_{Cu:Sn:Sn:Cu}^{4SL} = G_{Sn:Cu:Cu:Sn}^{4SL} = G_{Sn:Cu:Sn:Cu}^{4SL} = -2w_1 - 3w_2$

$D0_3$: $G_{Cu:Cu:Cu:Sn}^{4SL} = G_{Cu:Cu:Sn:Cu}^{4SL} = G_{Cu:Sn:Cu:Cu}^{4SL} = G_{Sn:Cu:Cu:Cu}^{4SL} =$

$G_{Sn:Sn:Sn:Cu}^{4SL} = G_{Sn:Sn:Cu:Sn}^{4SL} = G_{Sn:Cu:Sn:Sn}^{4SL} = G_{Cu:Sn:Sn:Sn}^{4SL} = -2w_1 - 1.5w_2$

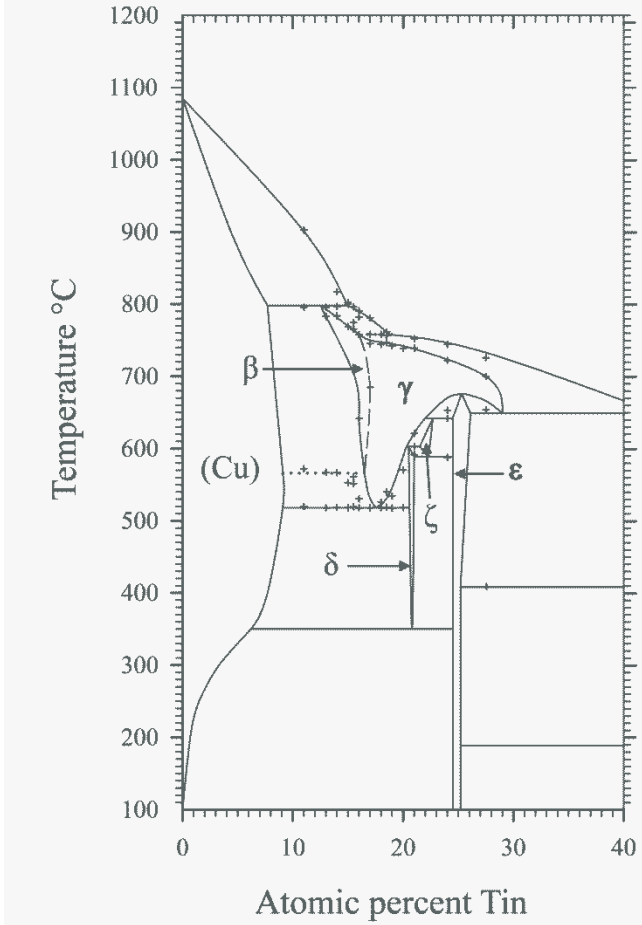


$D0_3$

Inden, G., Acta Metall., 1974. 22(8): 945-951.

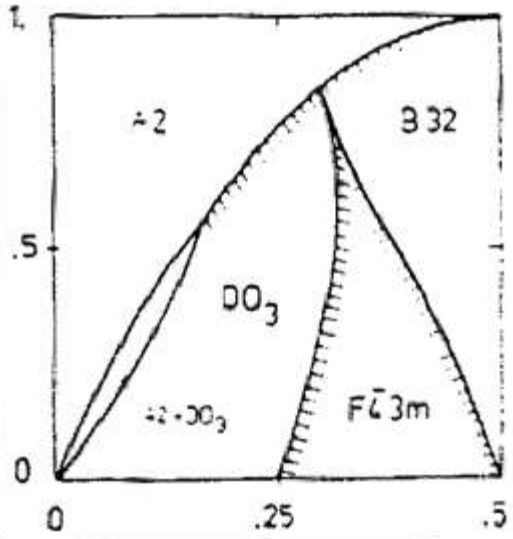
Modeling: w_1 to w_2 Ratio

Experimental results, submitted to Intermetallics

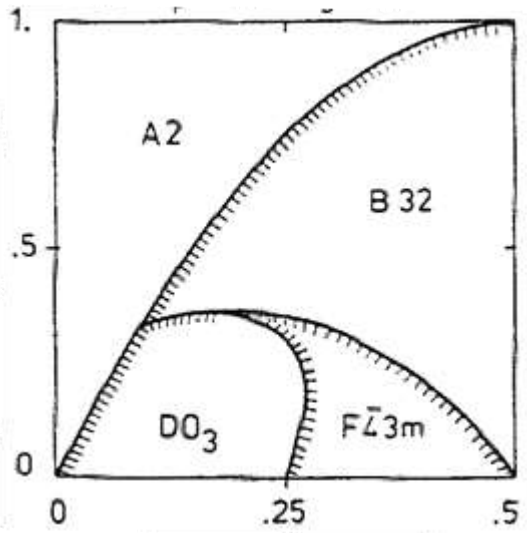


G. Inden, Acta Metall., 1974. 22(8): p. 945-951.

The ordering behavior can be determined by the ratio between w_1 and w_2



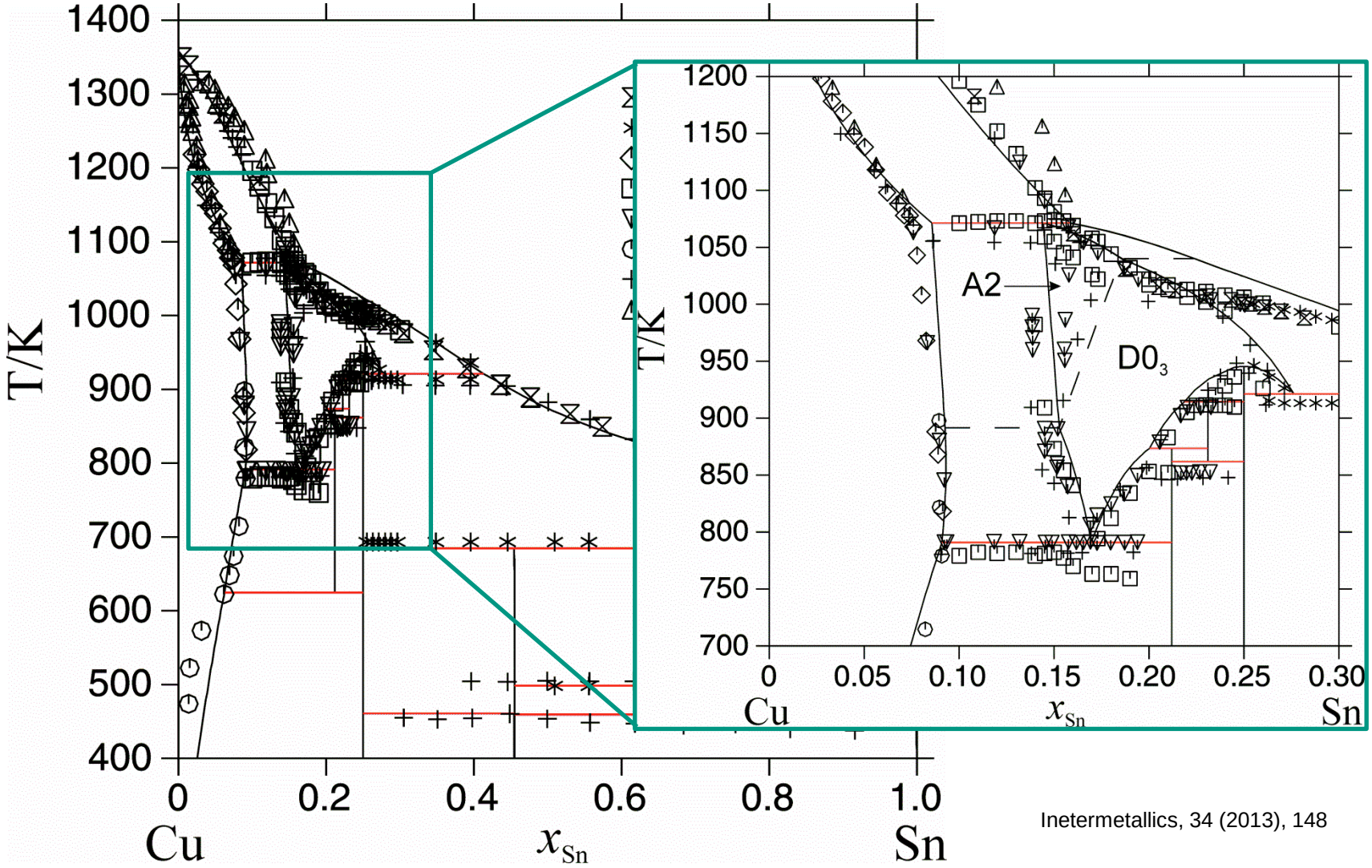
$w_1=w_2$



$w_1=0.5w_2$

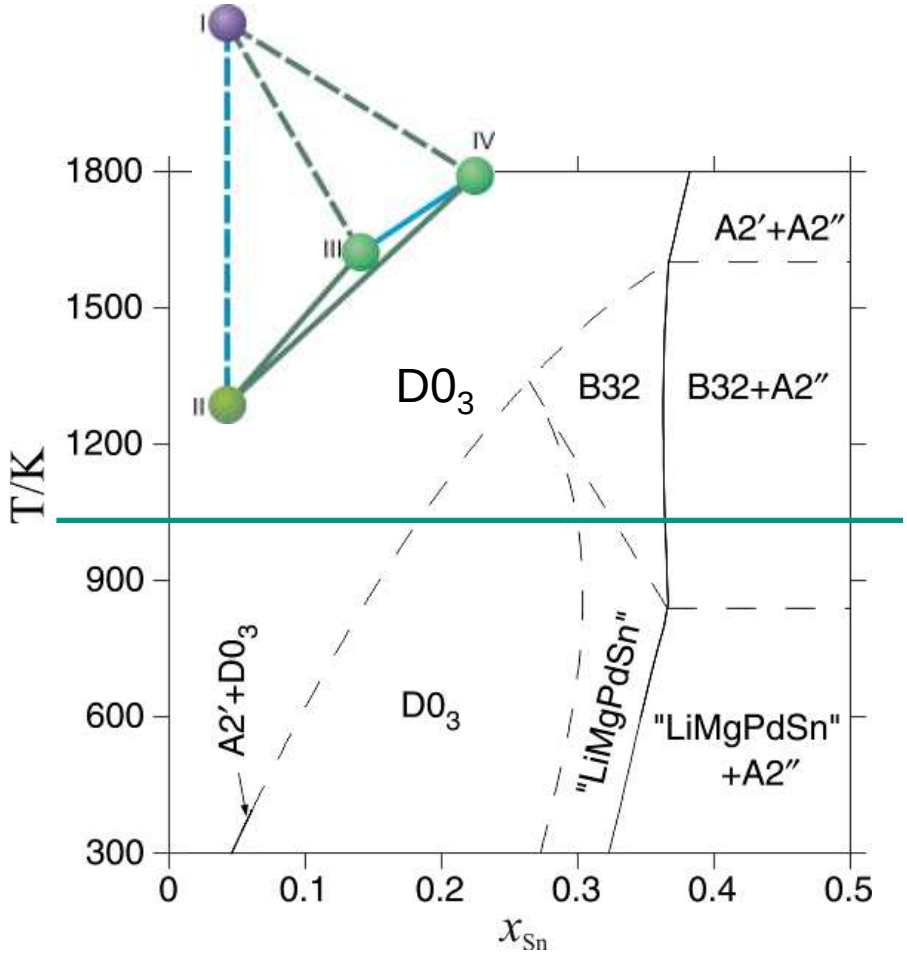
$w_1=0.9w_2$

Results (Cu-Sn)

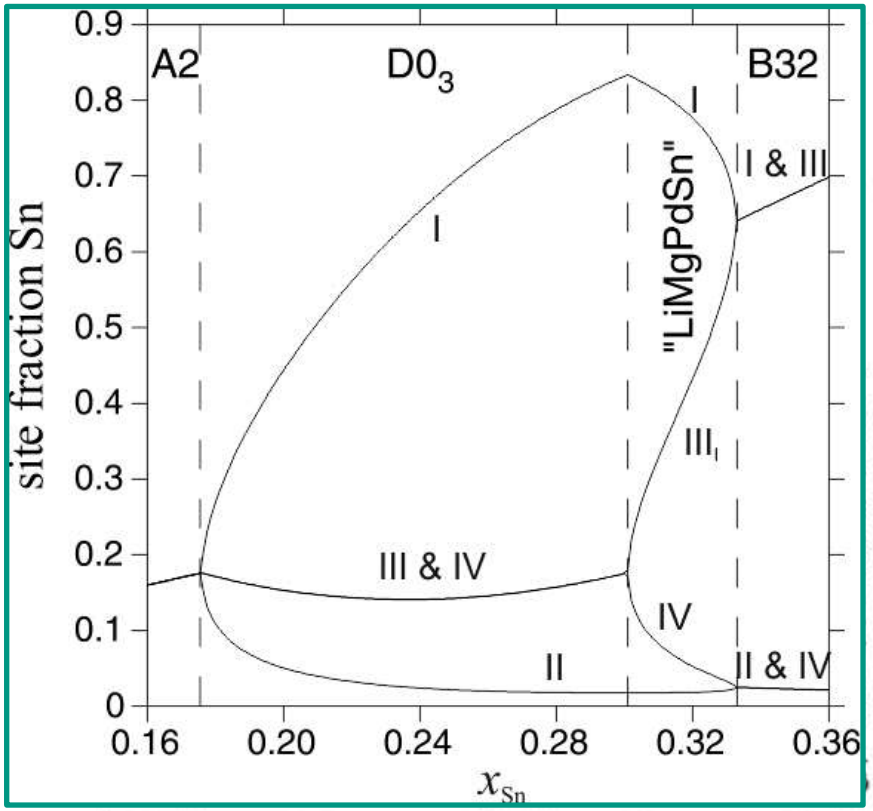


Inetermetallics, 34 (2013), 148

Results: BCC Ordering Map (Cu-Sn)

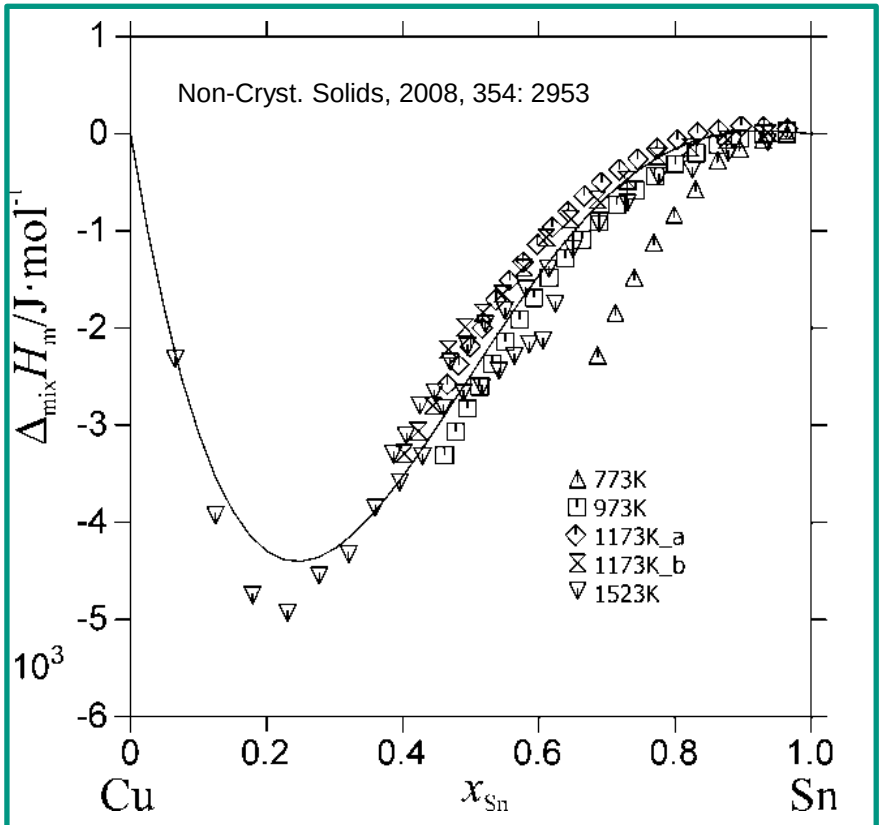


w_1=0.9w_2, this work

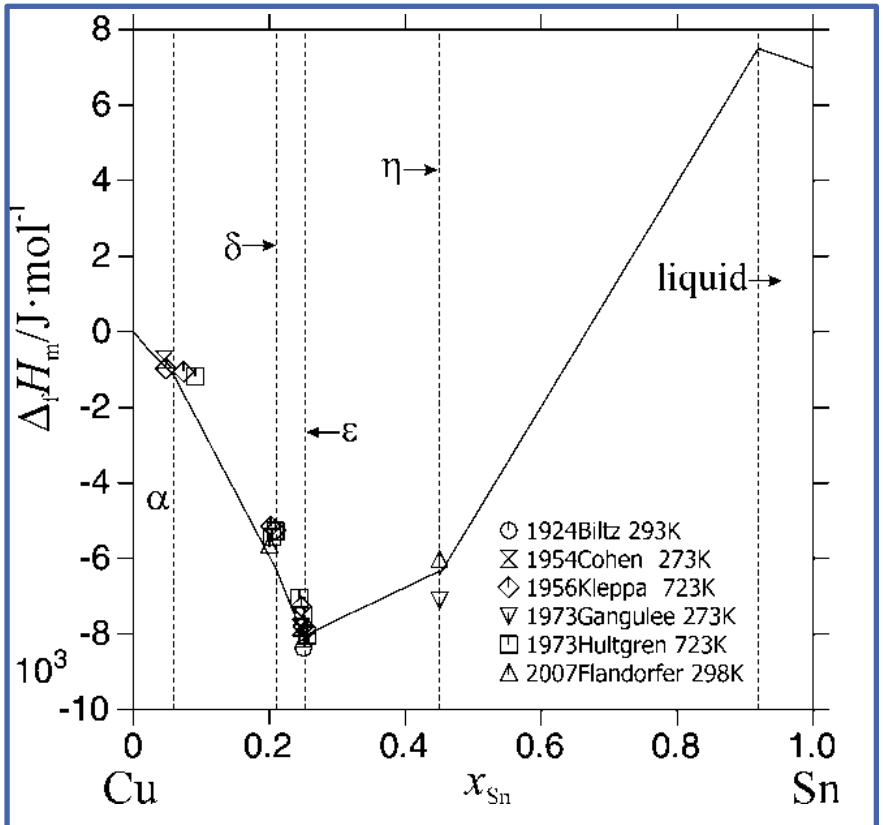


w_1=w_2, 1974Inden,
Acta Metall., 1974, 22, 945

Results: Enthalpies of Formation (Cu-Sn)

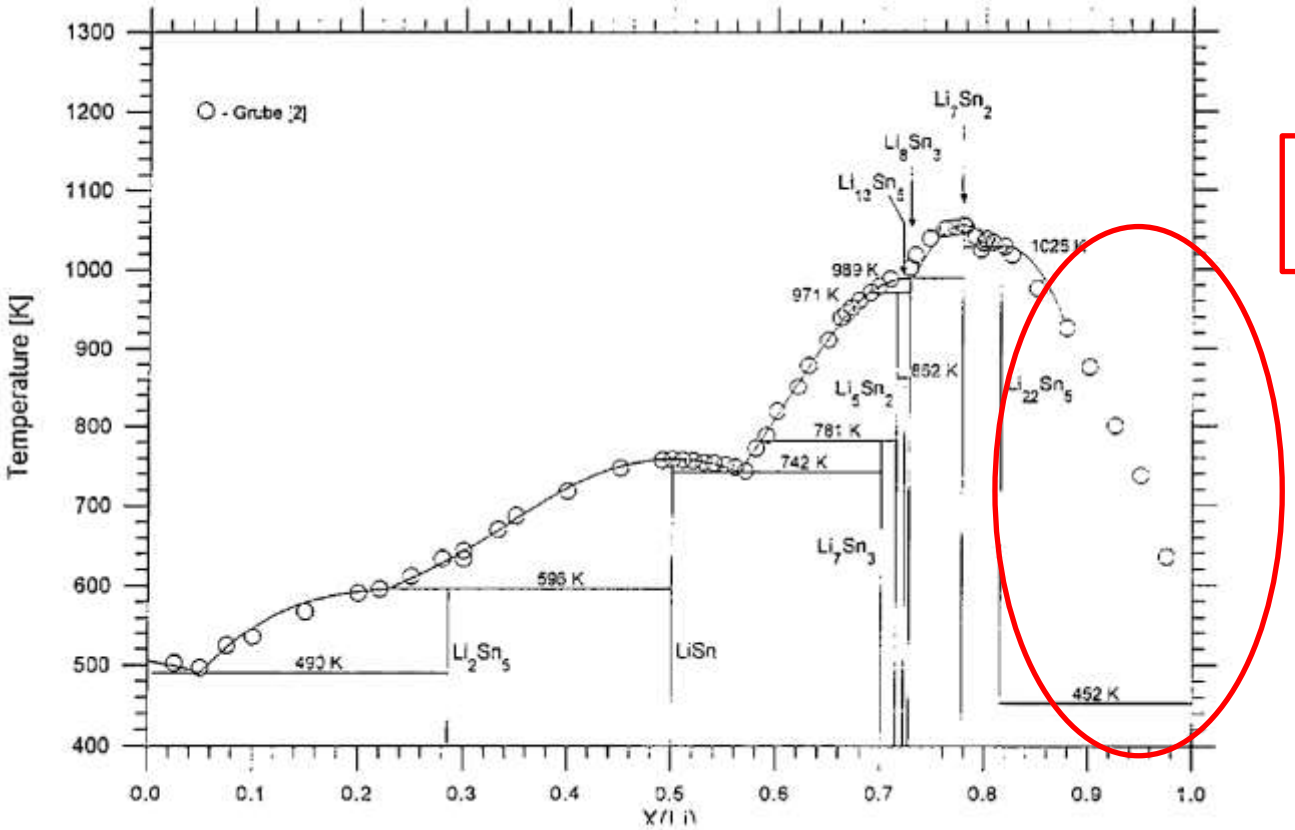


Liquid phase, *T*=1000 K, references state: liquid components



Stable phases, *T*=673K, references state: fcc(Cu) and bct(Sn)

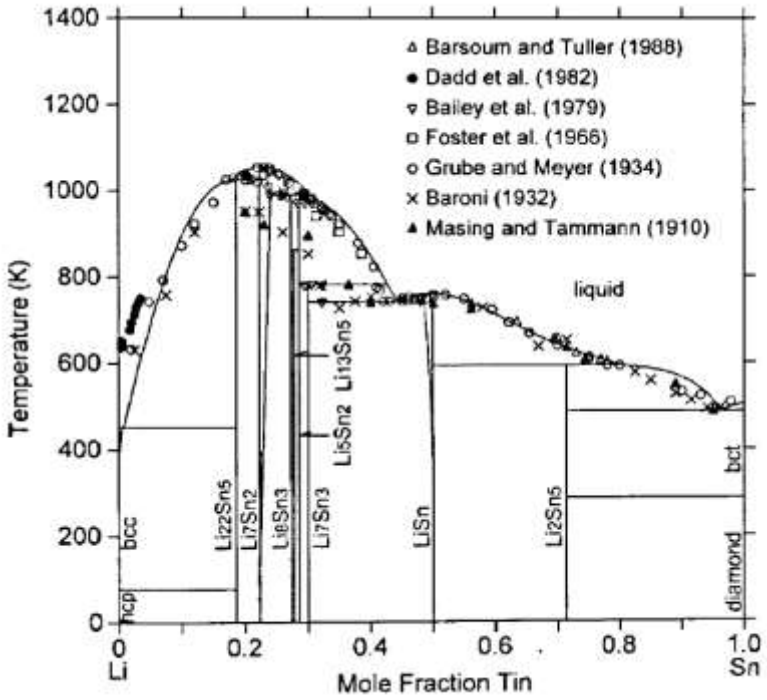
Thermodynamic Descriptions of the Li-Sn System

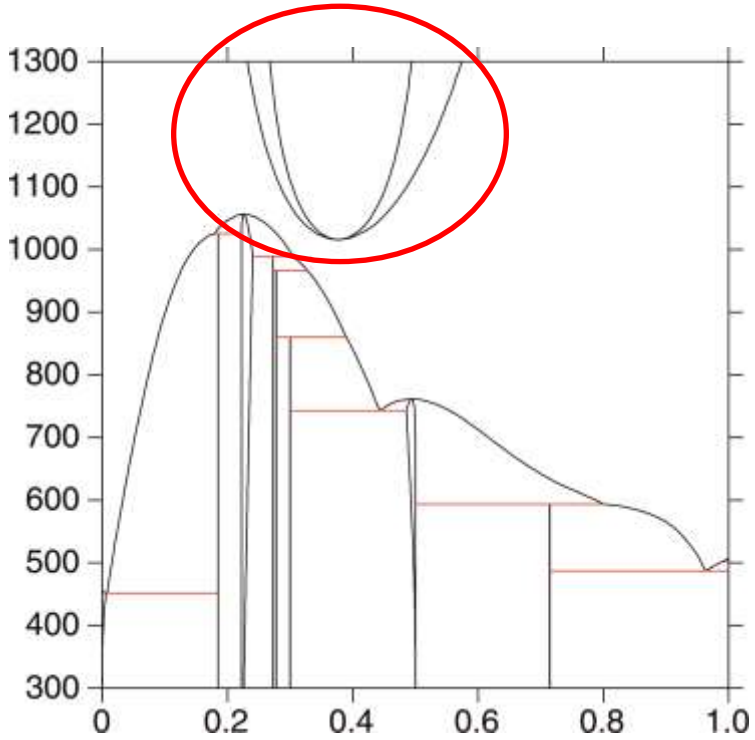


Can not reproduce the phase diagram

Gasior, W. et al. J. Non-Cryst. Solids, 1996. 205-207(1): 379-382.

Li-Sn Phase Diagram in Literature

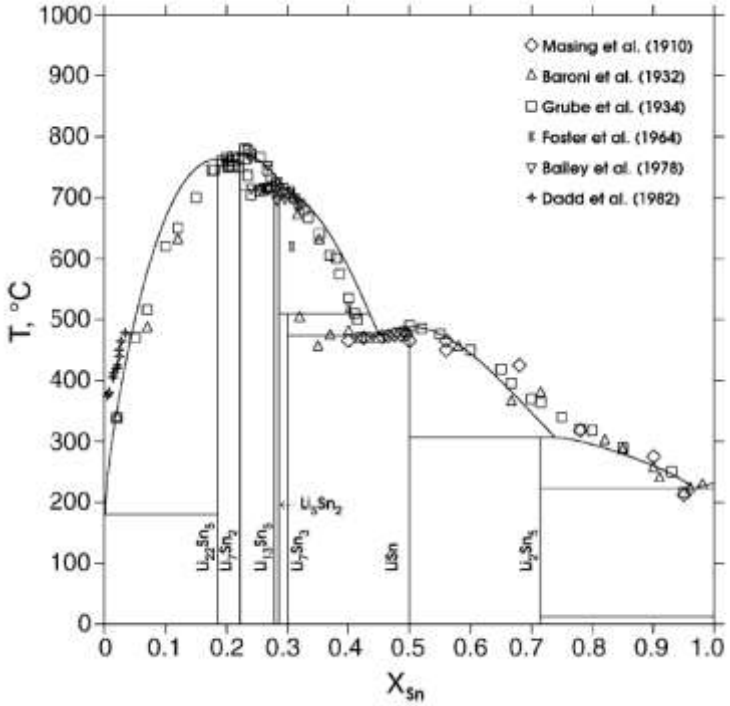




Du, Z. M., et al., Z. Metallkd., 2006, 97: 10-16.

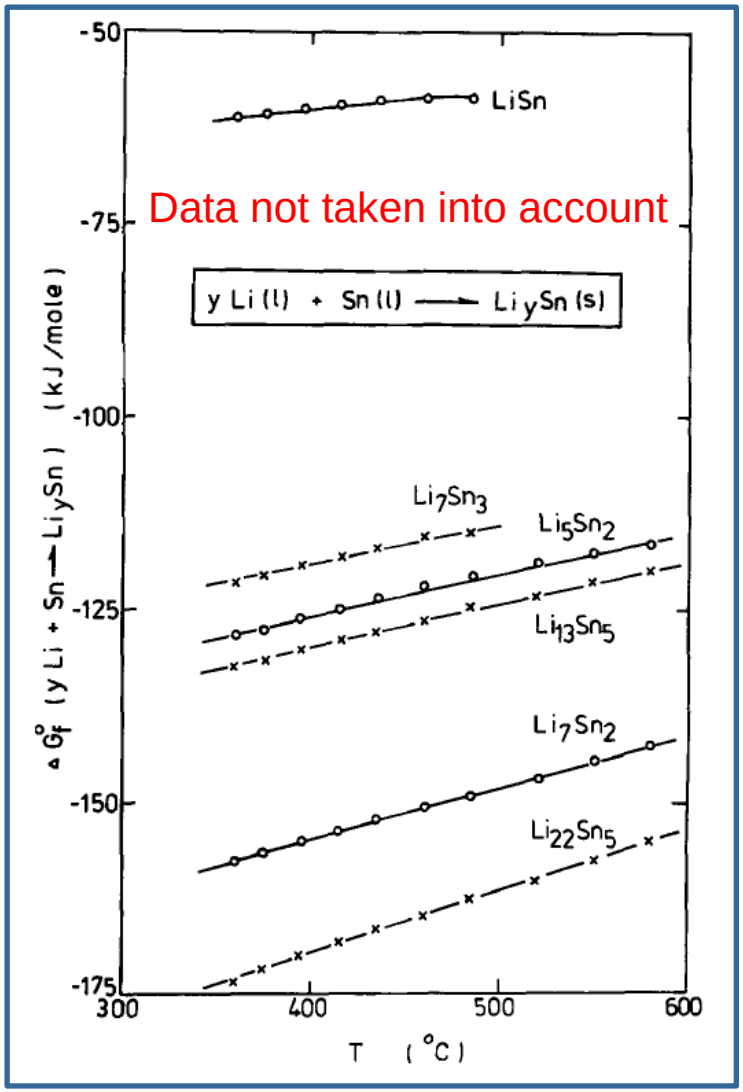
- Bcc phase stable at high temperature.
- Inverse miscibility gap in the liquid (not shown)
- Did not well reproduced mixing enthalpies of liquid phase

Previous Calculated Li-Sn Phase Diagrams



Yin, F., et al., J. Alloys Compd., 2005. 393(1-2): p. 105-108.

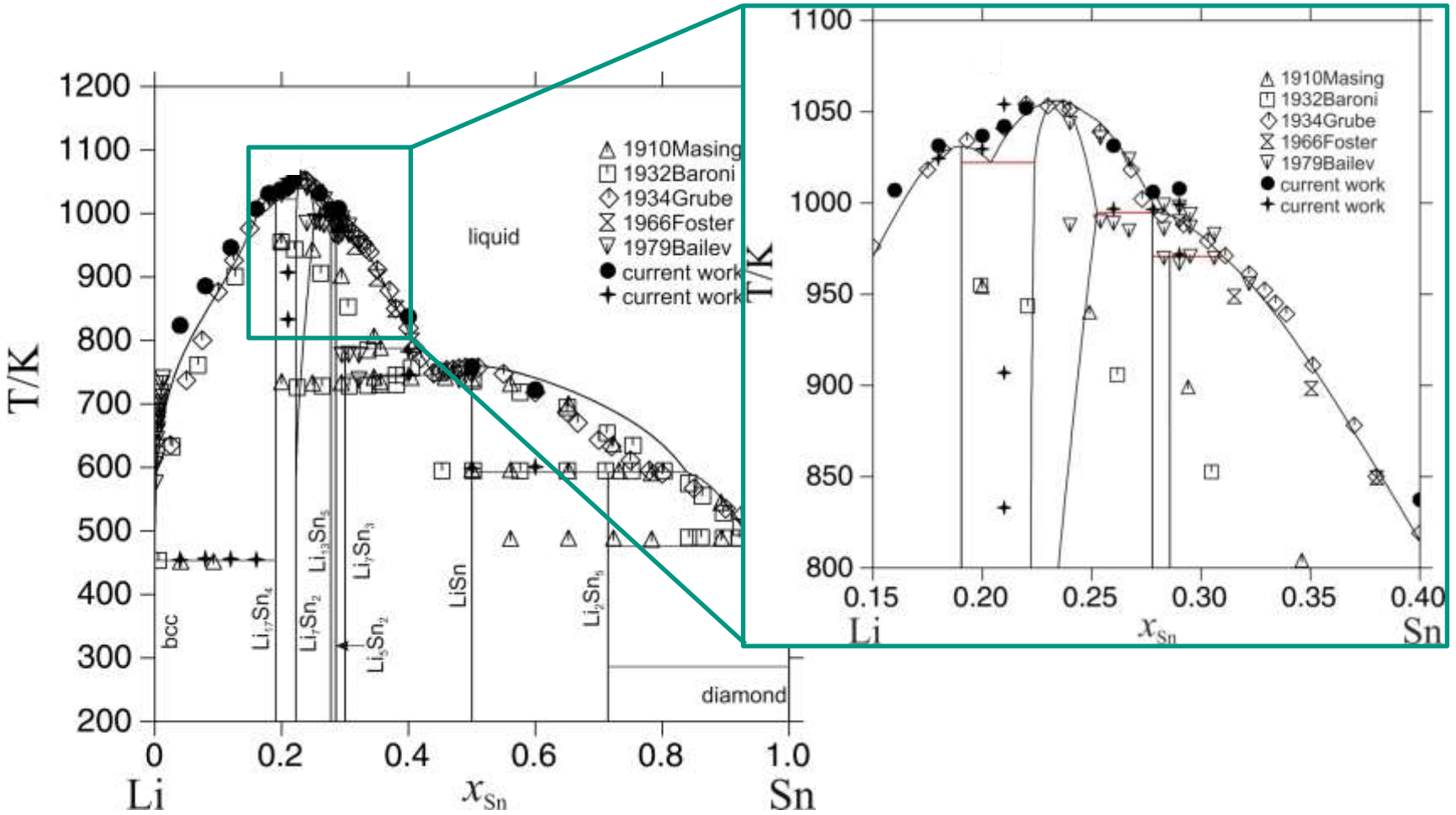
- Ignore important literature information. (Wen, C.J. and R.A. Huggins, J. Electrochem. Soc., 1981. 128(6): p. 1181-1187.)



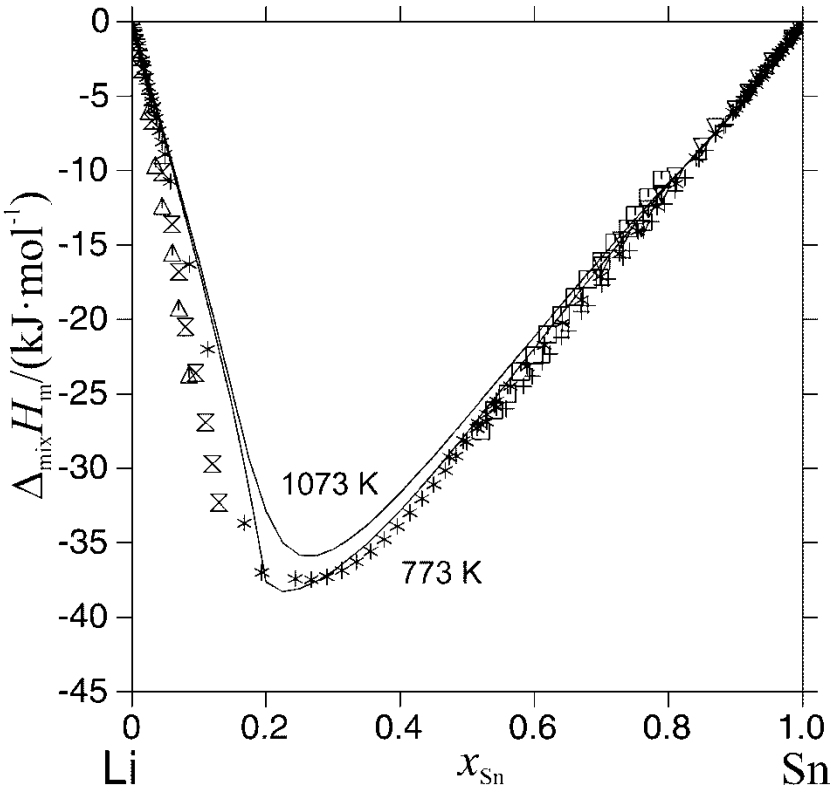
Key Information for Li-Sn System

- New calorimetry data (enthalpy of mixing in the liquid)
- New KEMS
- Phase diagram data
- Emf results (1981Wen)
- The associate formation in the liquid phase has been observed (J. Phys. F, 1984, 14(9), p. 1995–2006)
- Associate model (Li, Li_4Sn, Sn) applied for liquid phase

Results: Phase Diagram (Li-Sn)

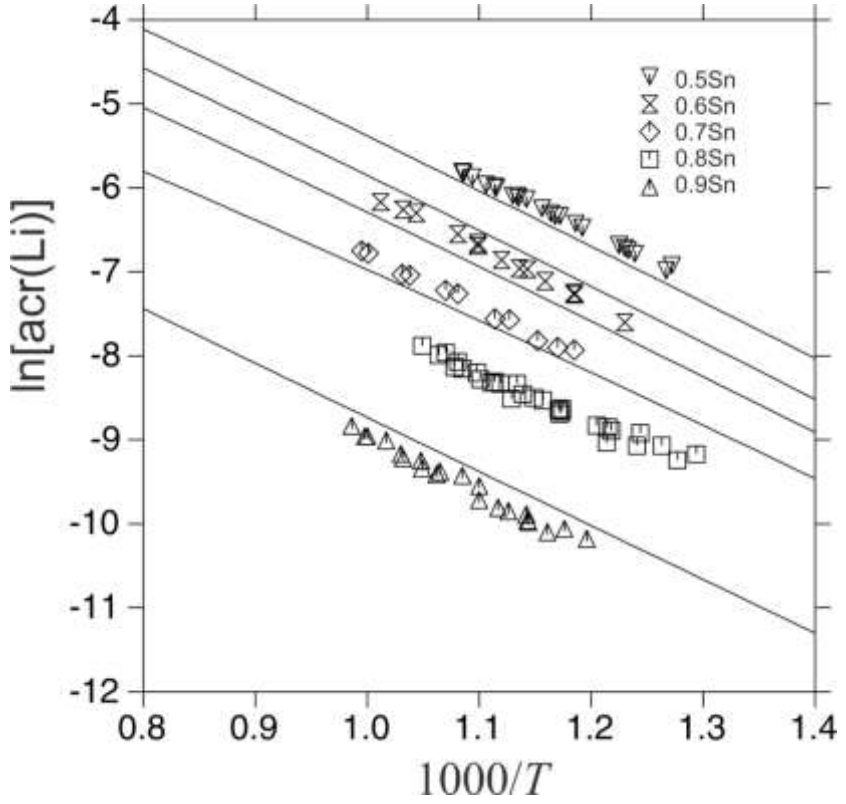


Results: Liquid Phase (Li-Sn)



Calorimetric measurement,

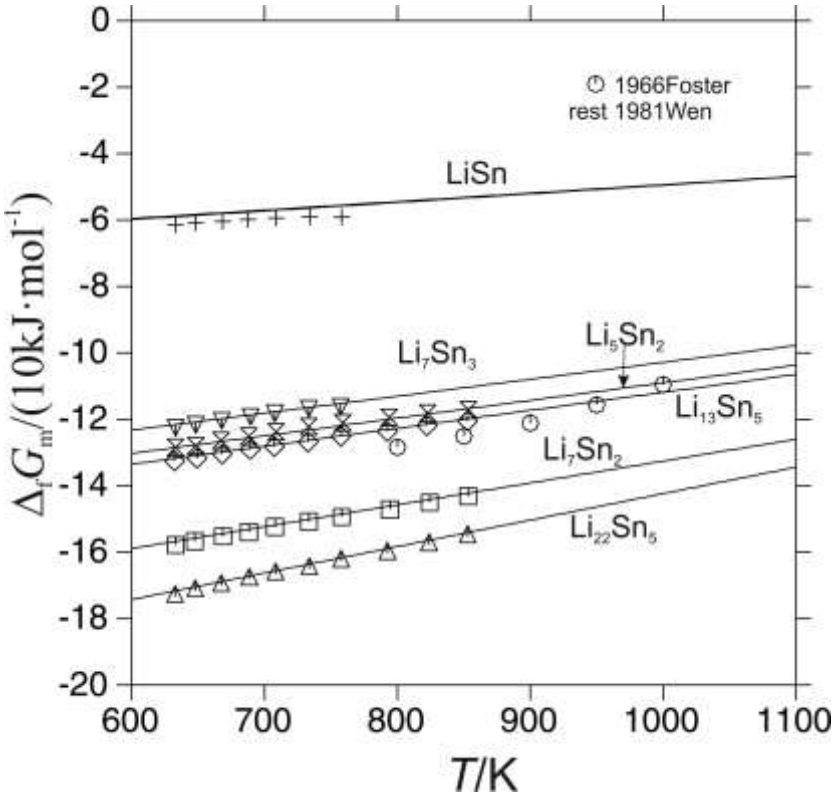
J. Chem. Thermodyn. , 2013, 61, 105



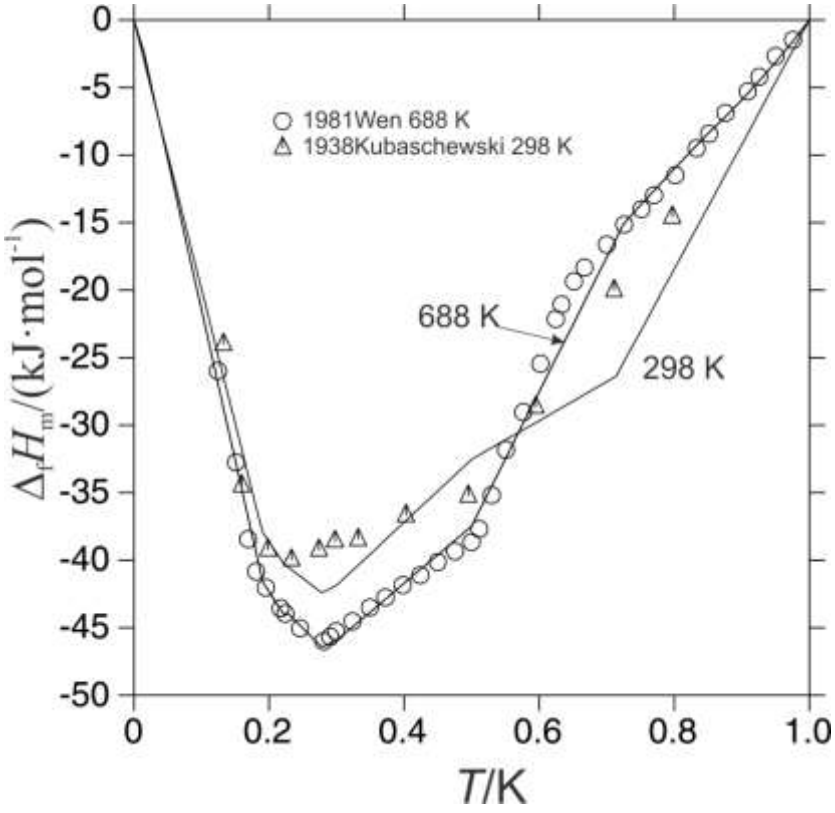
KEMS measurement,

Jülich, submitted

Results: Solid Phase (Li-Sn)

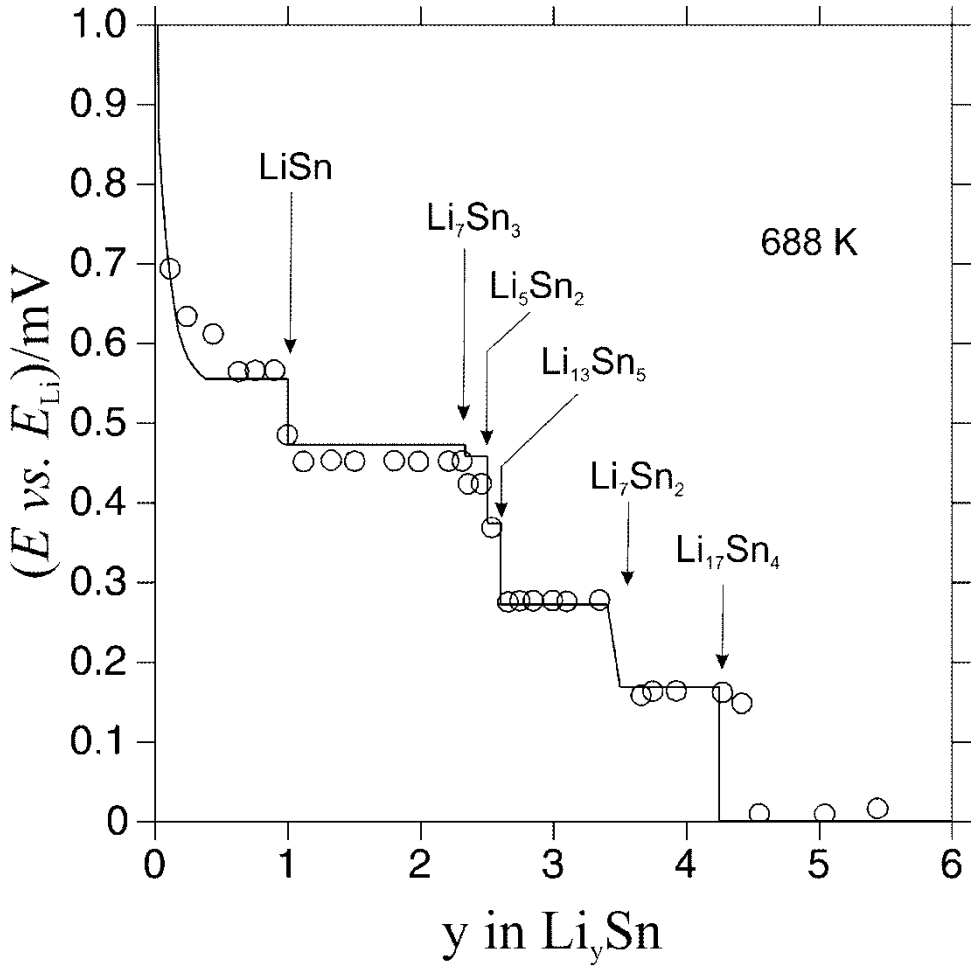


J. Electrochem. Soc., 1981, 128(6): 1181
J. Phys. Chem. , 1966, 70(10): 1042



J. Electrochem. Soc., 1981, 128(6): 1181
Z. Metallkd., 1938, 30: 7

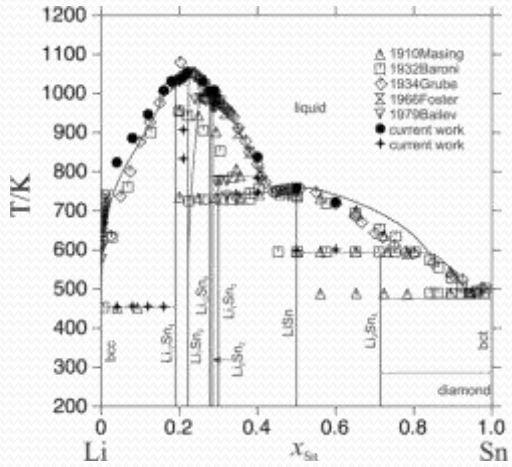
Results: E.m.f. Curve (Li-Sn)



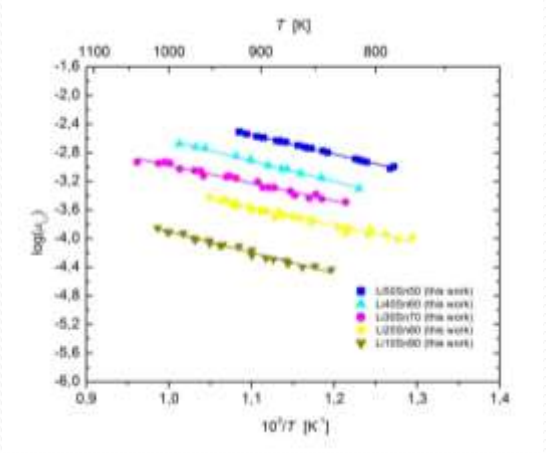
C.J. Wen and R.A. Huggins, J. Electrochem. Soc., 1981. 128(6): 1181

Assessment of Li-Sn based on KEMS, Calorimetry, XRD and DTA

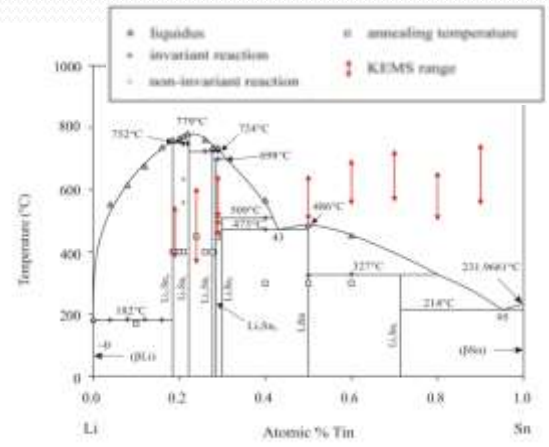
Sample preparation



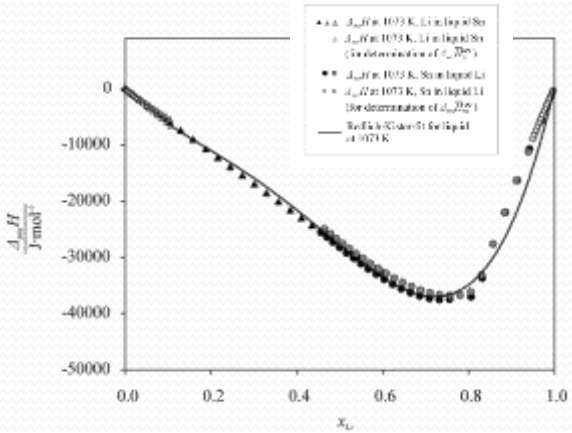
Optimized phase diagram



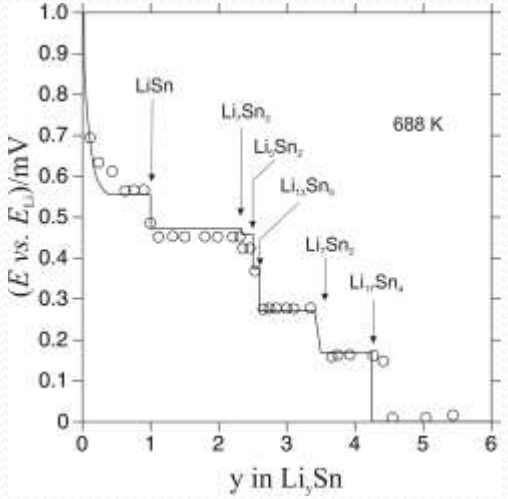
Temperature dependencies of Li activity (KEMS)



Experimental phase diagram



Mixing enthalpies (drop calorimetry)



Calculated EMF