Thermodynamic databases for lead free solders

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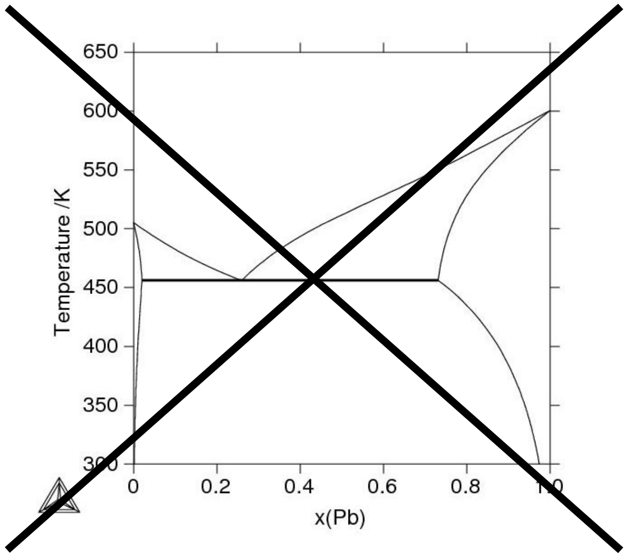
Outline

- Why lead-free solders?
- COST and COST Actions
- Database construction
- COST 531 & MP0602 databases for lead-free solders
  - Scope of databases
  - Modelling issues
  - Applications



So, why lead-free solders?

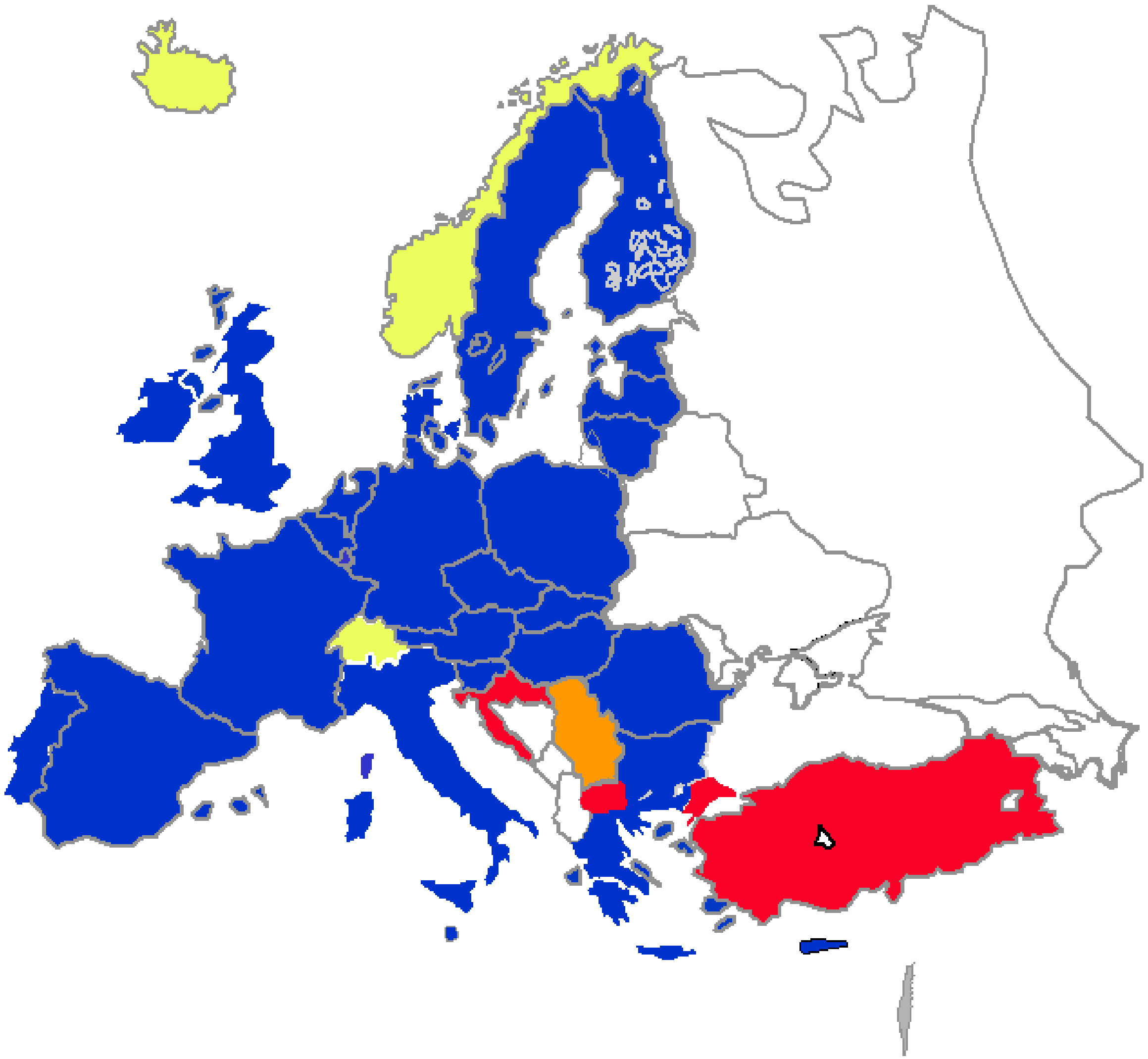
- Environmental issues
  - Toxic
  - Incorporated into bone marrow, nerve tissue, brain, kidneys..
  - Low levels affect the brain, central nervous system, lead to learning difficulties in children, impair physical and mental development
- Disposal of electrical and electronic equipment
  - Lead leaching into groundwater from landfill
- European legislation
  - Waste Electrical and Electronic Equipment (WEEE) Directive
  - Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment Regulations 2006 (RoHS) – 1st July 2006
- Solders
  - Conventional “electrician’s solder” already replaced
  - Need replacement for high temperature, high-Pb containing alloys
  - Currently exempt from RoHS legislation ….. but future EU legislation is likely

COST and COST Actions

What is COST ?

- European COoperation in the field of Scientific and Technical research
- Mission: To strengthen Europe in scientific and technical research for peaceful purposes through the support of cooperation and interaction between European researchers
- 34 COST member states plus 1 cooperating member
- Supported by the European Commission through the Framework Programme
- Works through a series of actions in the form of networked research projects
- Aims to coordinate nationally funded research at a European level

COST Countries



- **27 EU Member States**
- **Candidate countries**
  - Croatia*
  - Former Yugoslav Republic of Macedonia (FYROM)*
  - Turkey
- **EFTA Member States**
  - Iceland
  - Norway
  - Switzerland
- **Other European Countries**
  - Republic of Serbia*
- **COST Cooperating States**
  - Israel

COST531

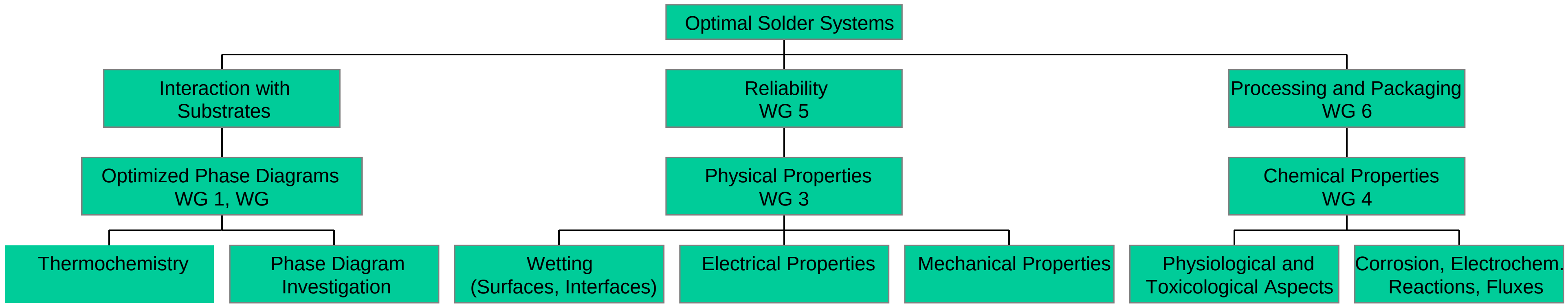
- A European Action on Lead-free Soldering (2002 to 2007)
- Coordinated by Herbert Ipser (University of Vienna)
- 45 research institutes from 17 countries
- Working Groups

  Groups 1&2: Thermochemistry and Phase Diagrams (Experimental + Modelling)

  Groups 3-6: Physical, Chemical Properties, Reliability Issues

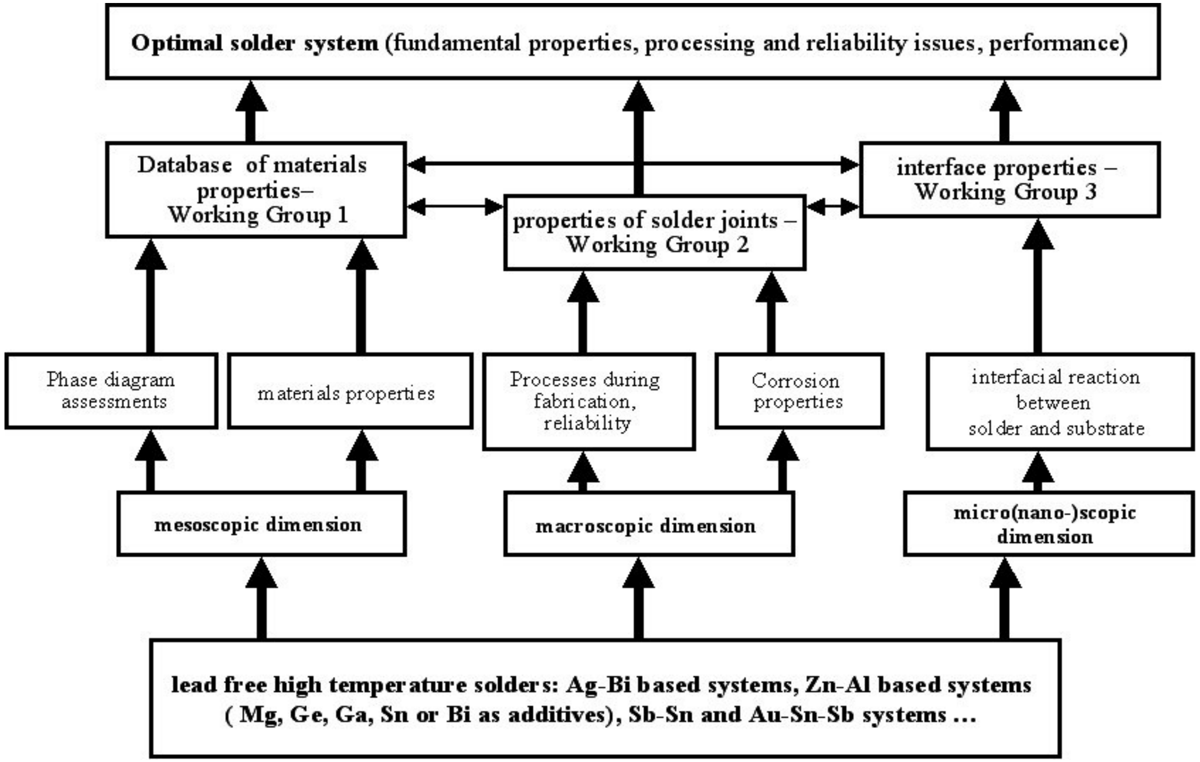
COST 531 – Lead-free Solder Materials: 2002-2007

"....to increase the basic knowledge on possible alloy systems that can be used as lead-free solder materials and to provide a scientific basis for a decision which of these materials to use for different soldering purposes in order to replace the currently used lead-containing solders in the future."



COST MP0602 - Advanced Solder Materials for High Temperature Application (HISOLD): 2007-2011

- *"...the investigation of Pb-free replacements for high-Pb solders for high-temperature applications..(using) a multiscale approach:* ***meso-scale:*** *The application of thermodynamics and kinetics; the development of materials property databases.*
- ***macro-scale:*** *The creation of a phenomenological description of corrosion and deformation processes occurring in a solder joint during fabrication and service,*
- ***micro- (nano-) scale:*** *The investigation by experiment and modelling of the initial stage of the formation of intermetallic phases at the solder/substrate interface....increase the basic understanding of alloys that can be used as Pb-free alternatives to high-temperature solders for practical applications.."*

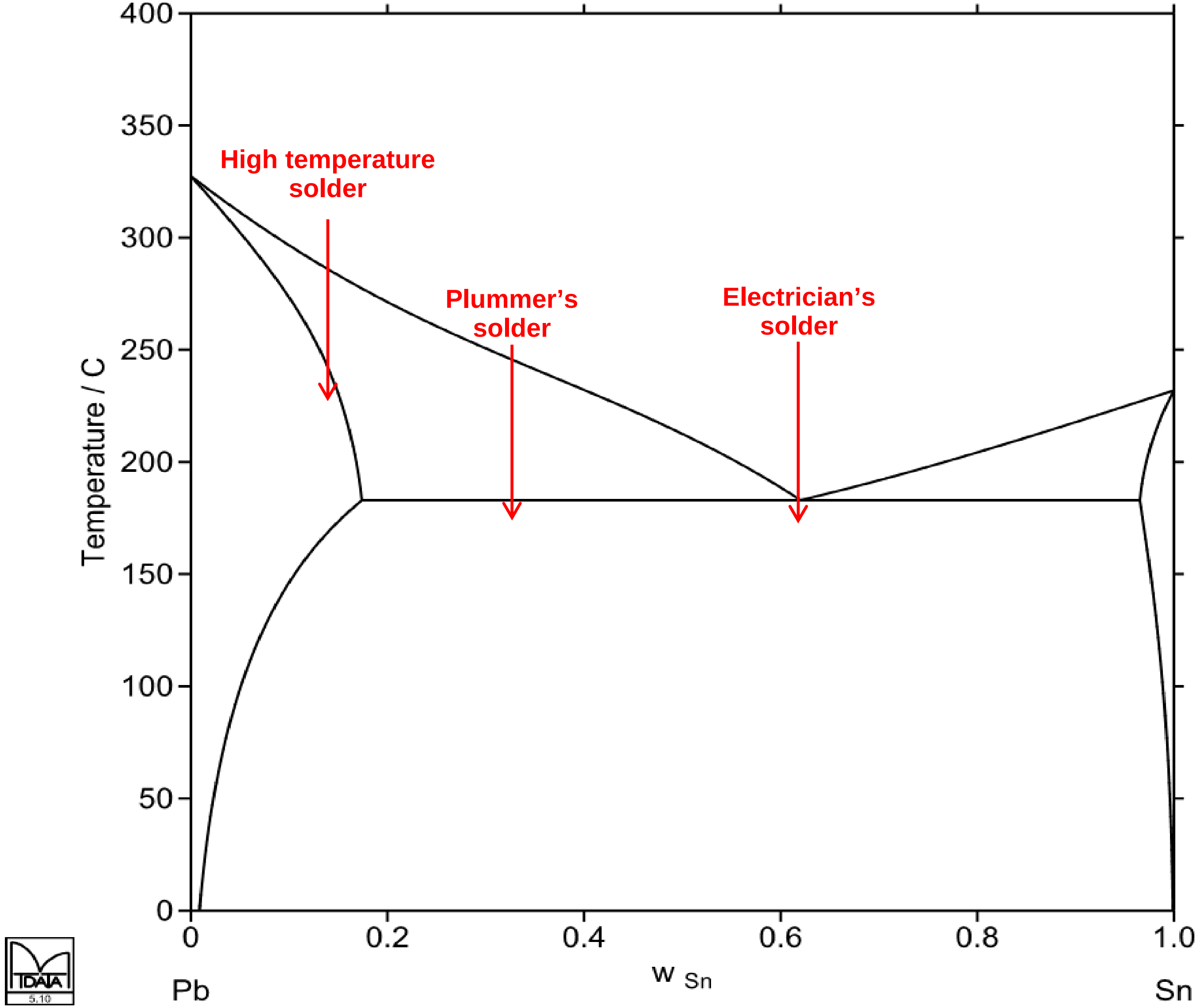


Coordinated by Ales Kroupa, Institute of Physics of Materials, Brno, Czech Republic

COST MP0602 - Advanced Solder Materials for High Temperature Application (HISOLD): 2007-2011

- Signatories
  - Austria
  - (Argentina)
  - Belgium
  - Bulgaria
  - Czech Republic*
  - Denmark
  - France
  - Finland
  - Germany
  - Hungary
  - Ireland
  - Italy
  - Netherlands
  - Poland
  - Portugal
  - Romania
  - (Russian Federation)
  - Serbia
  - Slovak Republic
  - Slovenia
  - Sweden
  - Switzerland
  - Turkey
  - (Ukraine)
  - United Kingdom

Pb-Sn phase diagram

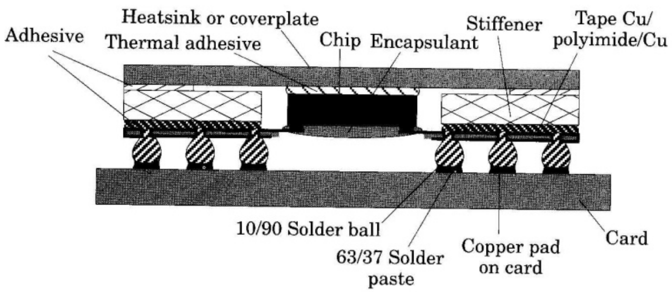


HISOLD: Main focus

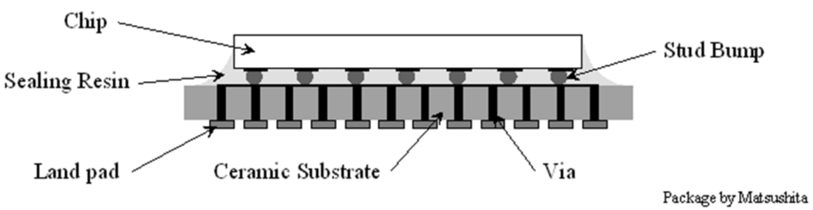
Replacement materials for high-temperature Pb-solders

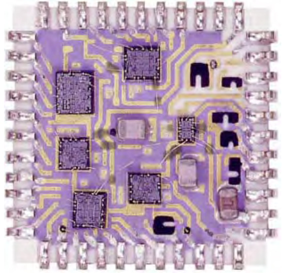
Solders with Tm ≥ 230°C – used in the electronics industry for advanced packaging technologies

Materials for BGA (Ball Grid Array) solder spheres



Materials for Chip Scale Packaging





Need for high temperature solders

- Power circuits

  very high levels of conductivity required

- Automotive industry under bonnet applications

  high current and low voltage, high temperatures within the engine area

- Multi-chip modelling (MCM)

  step soldering approach - soldering of various levels of the package with different solders of different melting points

  upper limit around 350°C (limit set by polymer used in substrate)

Pb-free high temperature solders required to replace current alloys for wide range of melting temperatures

Database construction

Database Construction: Sources of data

- SGTE solution database (SSOL)
    - (*Data sharing arrangement*)
- NPL Solders database
- Brno Solders database
    - (*Institute of Physics of Materials, Czech Academy of Sciences, Brno*)
- New assessments generated during the Actions
- Assessments in the open scientific literature
    - Reassessment often required
        - New experimental data generated during the Actions
        - New modelling
- Testing with MTDATA, ThermoCalc, Pandat

Database Construction: The need for internal consistency

- Unary data
  - Basis for all of the datasets within the database
  - SGTE Unary v4.4
    - Sn(fcc)
      - FUNCTION GFCCSN 100 5510 – 8.46*T + GHSERSN; 3000
    - Sn(hcp)
      - FUNCTION GHCPSN 100 3900 – 7.646*T + GHSERSN; 3000
  - SGTE Unary v1.1
    - Sn(fcc)
      - FUNCTION GFCCSN 100 4150 – 5.2*T + GHSERSN; 3000
    - Sn(hcp)
      - FUNCTION GHCPSN 100 3900 – 4.4*T + GHSERSN; 3000

Database Construction: The need for internal consistency

- Phase names
  - The same phase in each system *should* have the same name
    - FCC_A1, BCC_A2, HCP_A3, BCT_A5
    - CUIN_GAMMA
      - Cu-In
      - Ag-In
  - 'Common names'

Database Construction: The need for internal consistency

Phase Name	Common Name	Strukturbericht designation	Pearson Symbol
LIQUID	Liquid		
FCC_A1	(Ag)	*A*1	*cF*4
BCC_A2	β	*A*2	*cP*2
HCP_A3	ζ	*A*3	*hP*2
CUIN_GAMMA	γ	$D8_3$	*cP*52
AGIN2	$AgIn_2$	*C*16	*tI*12
TETRAG_A6	(In)	*A*6	*tI*2

Scope of databases

COST531 database

Scope: 11 elements

Ag, Au, Bi, Cu, In, Ni, Pb, Pd, Sb, Sn, Zn

Binary systems: All 55 binary systems except

Ni-Sb (now available) and Pd-Sb

Selected ternary systems:

Ag-Au-Bi, Ag-Au-Sb, Ag-Bi-Sn, Ag-Cu-Ni, Ag-Cu-Pb,

Ag-Cu-Sn, Ag-In-Sn, Ag-Ni-Sn

Au-Bi-Sb, Au-In-Sb, Au-In-Sn, Au-Ni-Sn

Bi-In-Sn, Bi-Sb-Sn, Bi-Sn-Zn

Cu-In-Sn, Cu-Ni-Pb, Cu-Ni-Sn

In-Sb-Sn, In-Sn-Zn

COST 531 database - Systems

- Assessed binary systems

  Ag-Au, Ag-Bi, Ag-Cu, Ag-In, Ag-Ni, Ag-Pb, Ag-Pd, Ag-Sb, Ag-Sn, Ag-Zn, Au-Bi, Au-Cu, Au-In, Au-Ni, Au-Pb, Au-Pd, Au-Sb, Au-Sn, Au-Zn, Bi-Cu, Bi-In, Bi-Ni, Bi-Pb, Bi-Pd, Bi-Sb, Bi-Sn, Bi-Zn, Cu-In, Cu-Ni, Cu-Pb, Cu-Pd, Cu-Sb, Cu-Sn, Cu-Zn, In-Ni, In-Pb, In-Pd, In-Sb, In-Sn, In-Zn, Ni-Pb, Ni-Pd, Ni-Sn, Ni-Zn, Pb-Pd, Pb-Sb, Pb-Sn, Pb-Zn, Pd-Sn, Pd-Zn, Sb-Sn, Sb-Zn, Sn-Zn

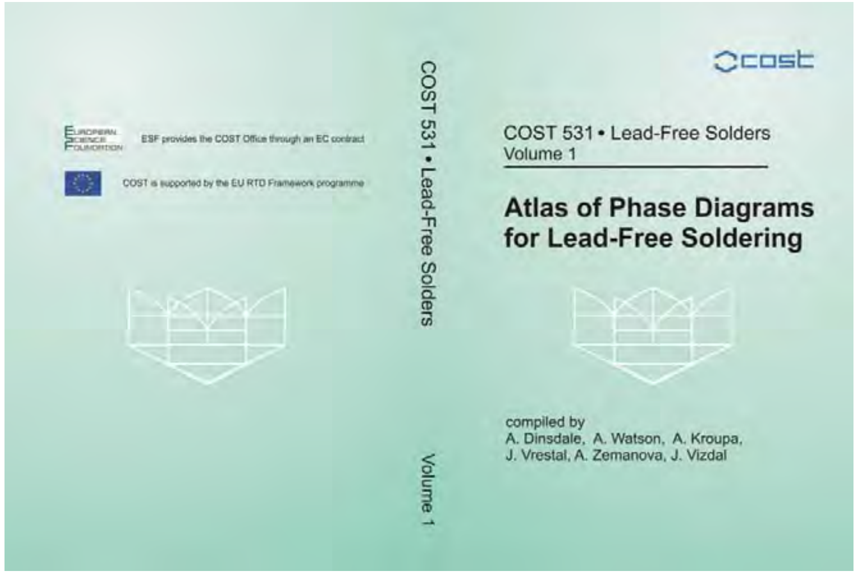
- Assessed ternary systems

  Ag-Au-Bi, Ag-Au-Sb, Ag-Bi-Sn, Ag-Cu-In*, Ag-Cu-Ni, Ag-Cu-Pb, Ag-Cu-Sn, Ag-In-Sn, Ag-Ni-Sn, Au-Bi-Sb, Au-In-Sb, Au-Ni-Sn, Bi-In-Sn, Bi-Sb-Sn, Bi-Sn-Zn, Cu-In-Sn, Cu-Ni-Sn, In-Sb-Sn, In-Sn-Zn

The “Atlas of Solders Phase Diagrams”

National Physical Laboratory

- The “Atlas of Phase Diagrams for Lead-Free soldering” has been published …. based on the data in the COST531 database



Bi-Zn system

Several authors worked on the theoretical description of the Bi-Zn system – e.g. Malakhov [00Mal], Oleari et al. [55Ole], Bale et al. [77Bal], Girard [85Gir] nebo Wang et al. [93Wan]. Kim and Sanders [03Kim] attempted to describe properly the segregation region in the liquid, using two interaction parameters LIZ only instead of six used by Malakhov. Unfortunately, their description is not consistent with unary parameters ( ) of the „COST531" database and therefore the data from Malakhov [00Mal] were used for this system. The changes of unary data were introduced and new value of G(HCP_ZN,BI:VA;0) from work of Moelans [03Moe] was accepted. New data were also introduced to model new experimental data from Vizdal et al. [07Viz] for solubility of Bi in HCP_ZN Zn (G(HCP_ZN,BI,ZN:VA;0)).

References:

[55Ole] Oleari, L., Fiorani, M., Valenti, V.: La Metallurgia Italiana, 1955, vol. 46, p. 773.

[77Bal] Bale, C. W., Pelton, A. D., Rigaud, M.: Z. Metallkd., 1977, vol. 68, p. 69.

[85Gir] Girard, C.: Ph.D. Thesis, Universite de Provence, Marseille, 1985

[93Wan] Wang, Z. C., Yu, S. K., Sommer, F.: J. Chimie Phys. Physico-Chimie Biol., 1993, vol. 90, p. 379.

[00Mal] Malakhov, D. V.: CALPHAD, 2000, vol. 24, p. 1

[03Kim] Kim, S. S., Sanders, T. H. Jr.: Z. Metallkd., 2003, vol. 94, p. 390.

[03Moe] Moelans, N., Kumar, K. C. H., Wollants, P.: J. All. and Comp., 2003, vol. 360, p. 98.

[07Viz] Vizdal, J., Braga, M. H., Kroupa, A., Richter, K. W., Soares, D., Malheiros, L. F., Ferreira, J.: CALPHAD – sent for publication, 2007

Table of invariant reactions

T / °C	Phases			Compositions / x_{Bi}		
254.5	RHOMBO_A7	LIQUID	HCP_ZN	0.016	0.081	0.998
271.4	LIQUID	RHOMBO_A7				
418.3	LIQUID 1	LIQUID 2	HCP_ZN	0.374	0.992	0.996
419.5	HCP_ZN	LIQUID				

Phase information

Phase Name	Common Name	Structure Type	Pearson Symbol
LIQUID	Liquid		
RHOMBO_A7	(Bi)	A7	hR2
HCP_ZN	(Zn)	A3 mod	hP2

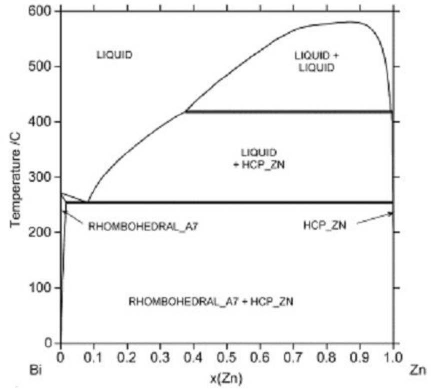


Fig. 1: ...

COST MP0602 - Scope

- Material under consideration
  - the high temperature solder
  - the substrate or contact material e.g. Cu, Ni-P, Pd
  - any legacy solder joint e.g. Pb-Sn
- Key solder systems identified
  - Zn-Al with Mg, Ge, Ga, Bi, Sn
  - Sn-Sb with Bi, Ag, Cu
  - Ag-Bi with Au, Sn
  - Au-Sn with Ag, Ge, Si
  - Zn-Sn with Bi, Ag, Cu

Ag, Al, Au, Bi, Co, Cu, Ga, Ge, In, Mg, Ni, P, Pb, Pd, Sb, Si, Sn, Ti, Zn

Final scope of the database

- …… the following set of systems for study

  Ag-Cu-Ni-P-Pb-Pd-**Sn**

  Al-Cu-Ga-Ge-Mg-Ni-P-Pb-Pd-Sn-**Zn**

  Bi-**Co-**Cu-Ni-P-Pb-Pd-Sn-**Ti**

  Ag-Au-Cu-Ni-P-Pb-Pd-**Sb-Sn**-Zn

  Ag-Bi-Cu-Ga-Ni-P-Pb-Pd-Sn

  Cu-Ni-P-Pb-Pd-**Sn-Zn**

- Please note

  Contains new elements eg Al, Co, Ga, Ge, Mg, P, Ti

  …. *but* leaves out In and systems such as Au-Bi, Bi-Sb and Bi-Zn

Modelling issues

Database Construction: The need for internal consistency

- Models
  - Gamma brass
    - Cu-Zn
      - Cu_5Zn_8
        - *cI*52, *D*8_2
    - Al-Cu
      - Cu_9Al_4
        - *cP*52, *D*8_3

Database Construction: The need for internal consistency

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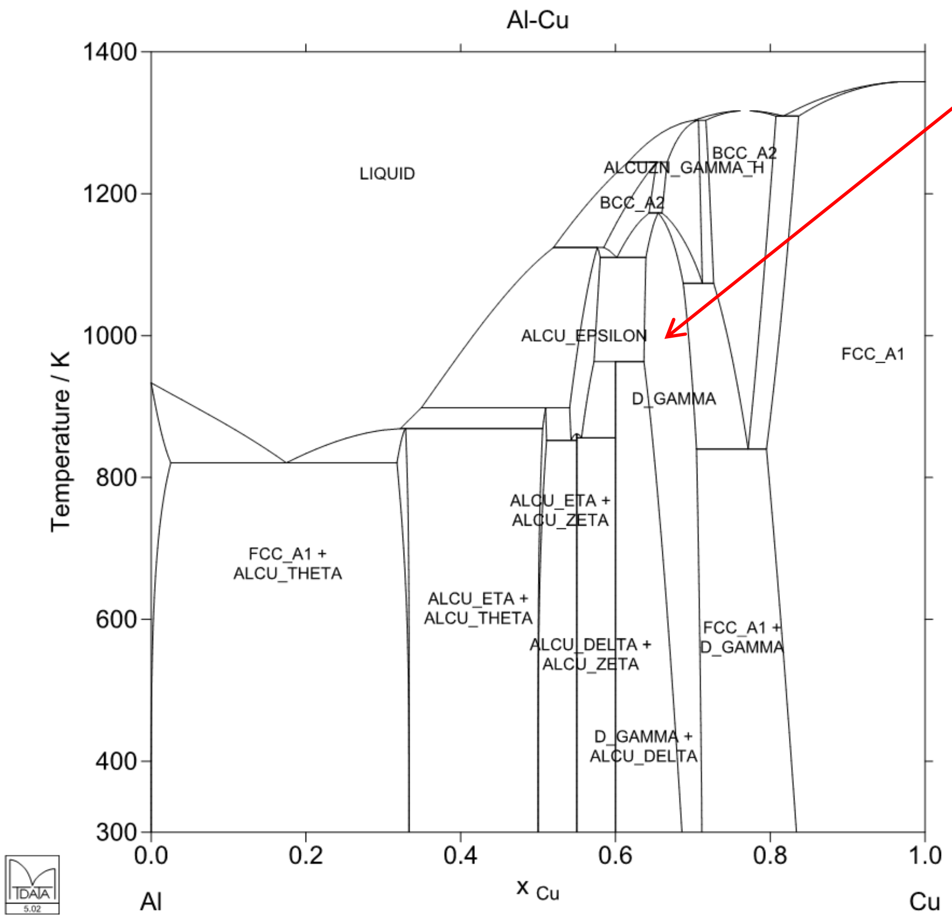

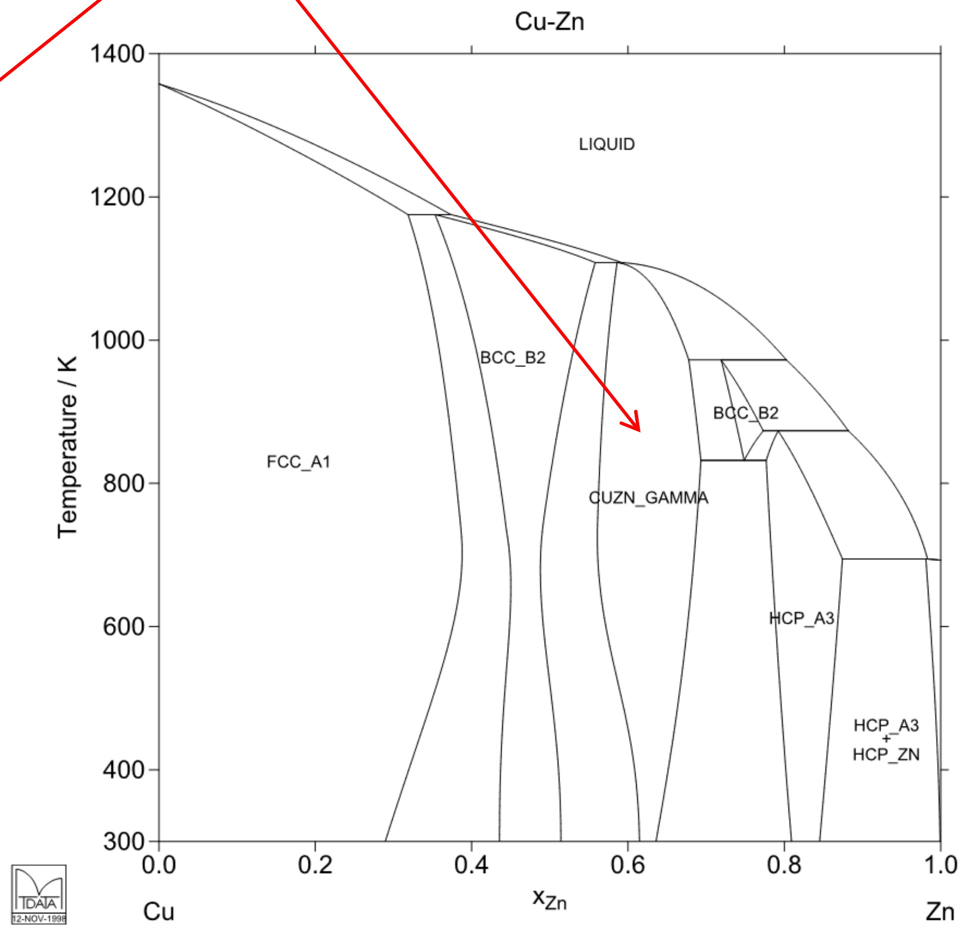

AL : AL CU : CU :

CU,ZN : CU,ZN : CU,ZN :CU,ZN :

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Assessed Experimental Al-Cu-Zn Phase Diagram

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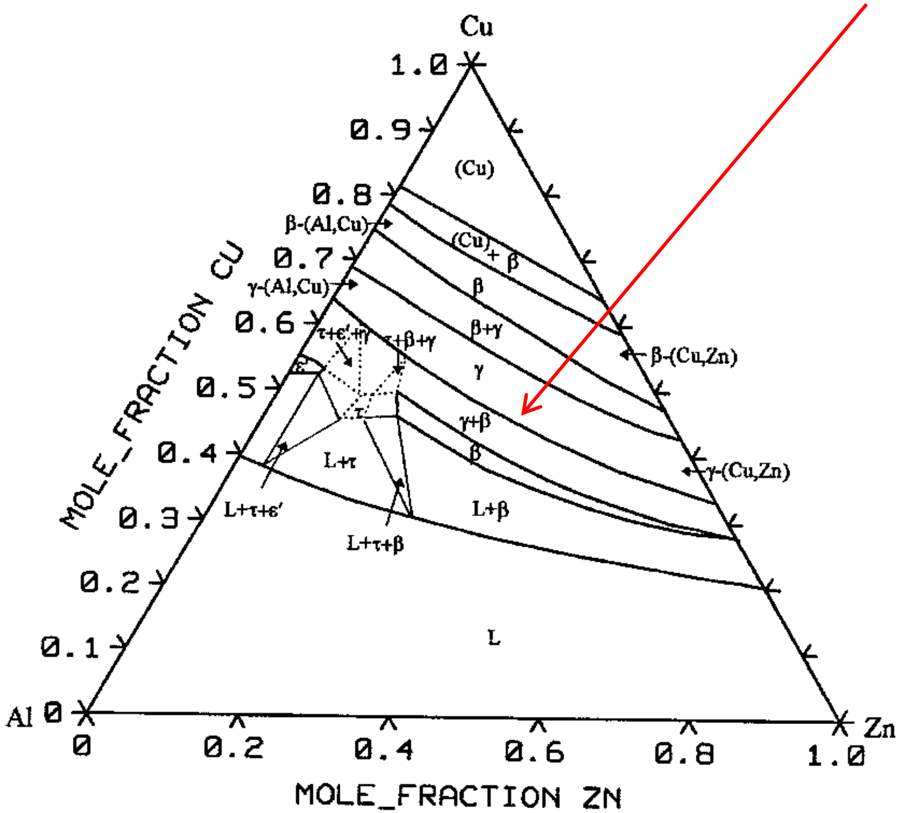
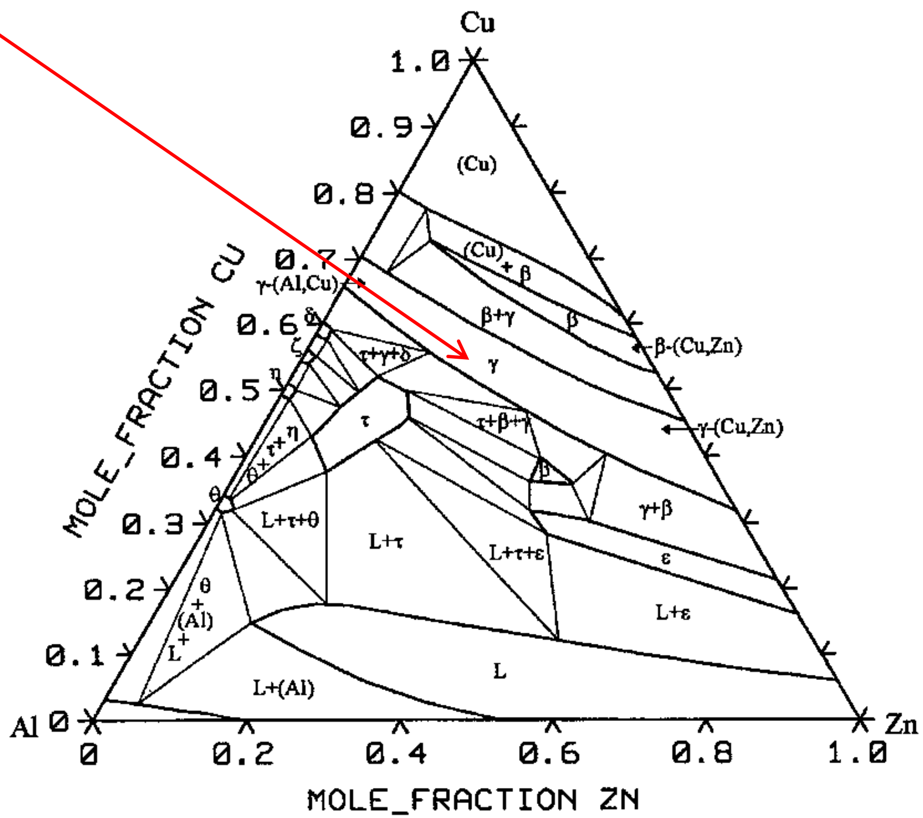
Gamma brass

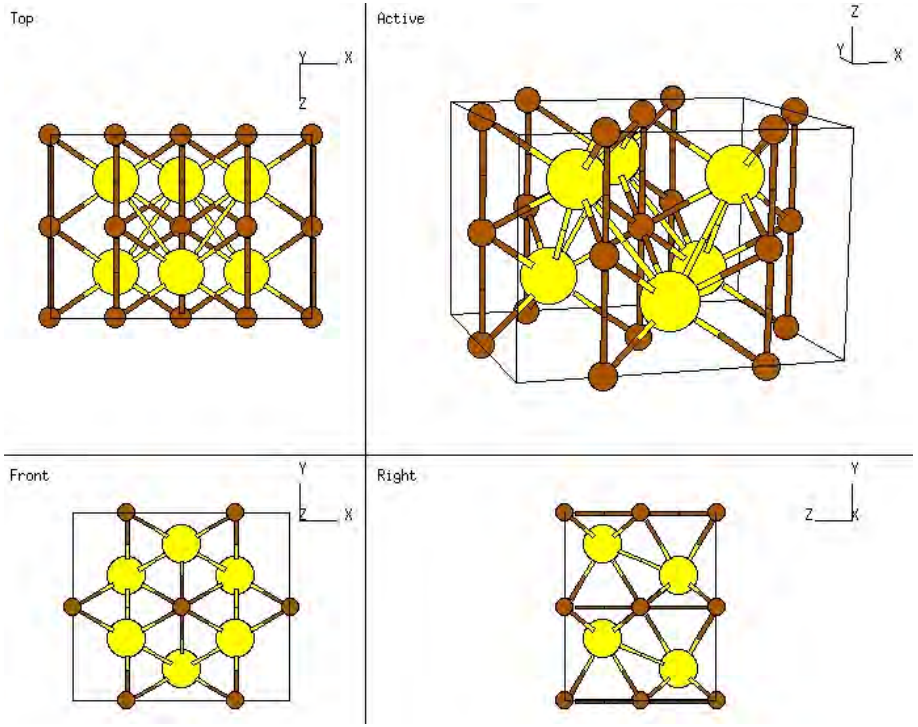


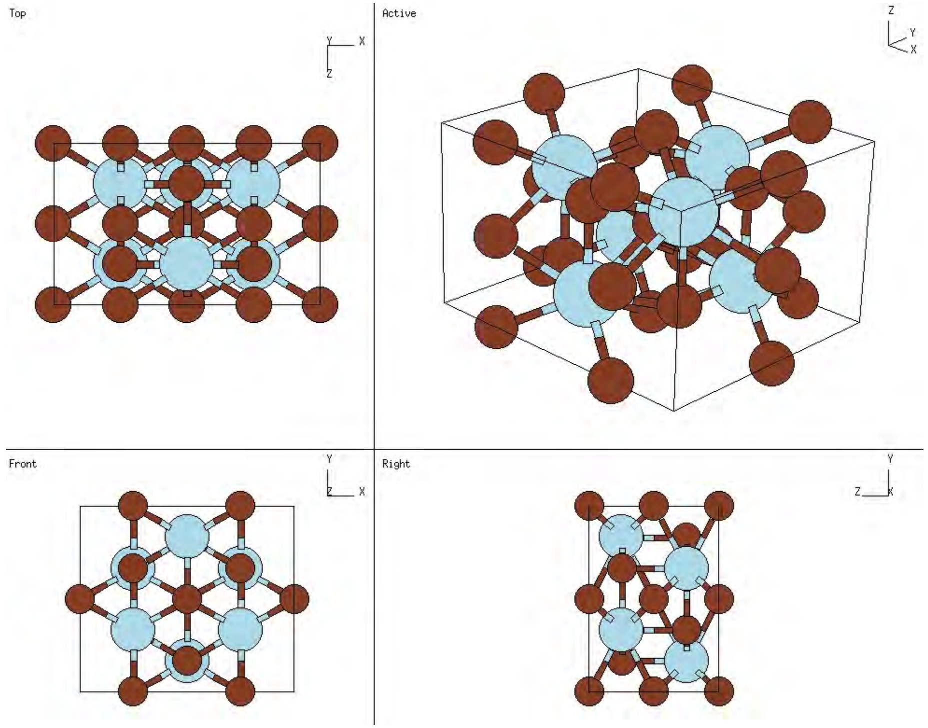
973K



773K

Database Construction: The need for internal consistency





NiAs prototype
Pearson symbol h*P*4

Ni_2In prototype
Pearson symbol h*P*6

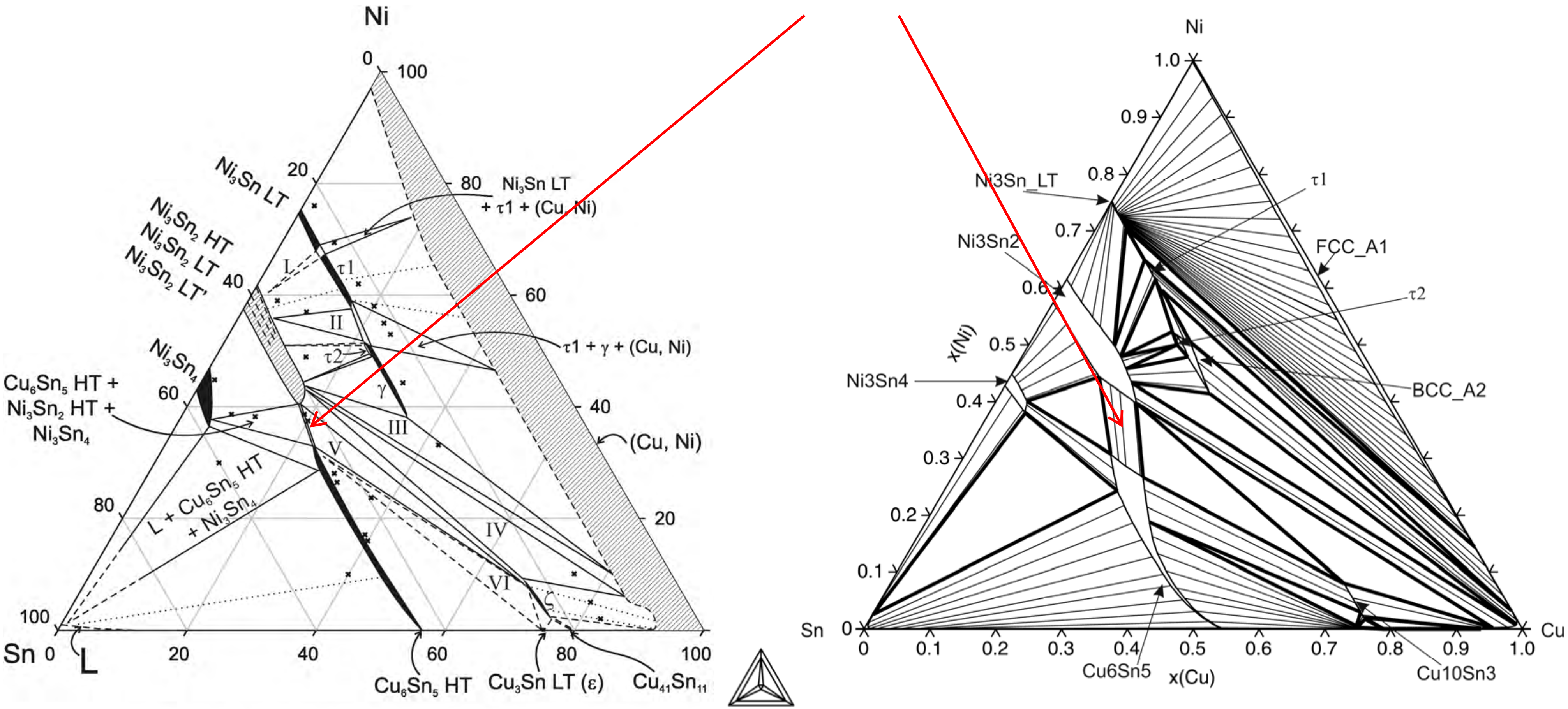
Thermodynamic models: NiAs and Ni_2In structures

- Cu_6Sn_5 phase has NiAs type structure (hP4)
  - particularly important, formed readily at the interface between Sn based solder and Cu substrate
- Ni_3Sn_2 has a structure based on the Ni_2In prototype (hP6)
  - Closely related to NiAs structure
- In Cu-Ni-Sn system
  - Ni dissolves appreciably in the Cu_6Sn_5 phase
  - Cu dissolves in Ni_3Sn_2
  - appears that the two phases do not form a continuous series of solid solutions
- Same situation in In-Ni-Sb system where there is a complete solubility between Ni_2In and NiSb

(Cu,Ni)(Cu,Ni,Va)(Sn)

Database Construction: The need for internal consistency

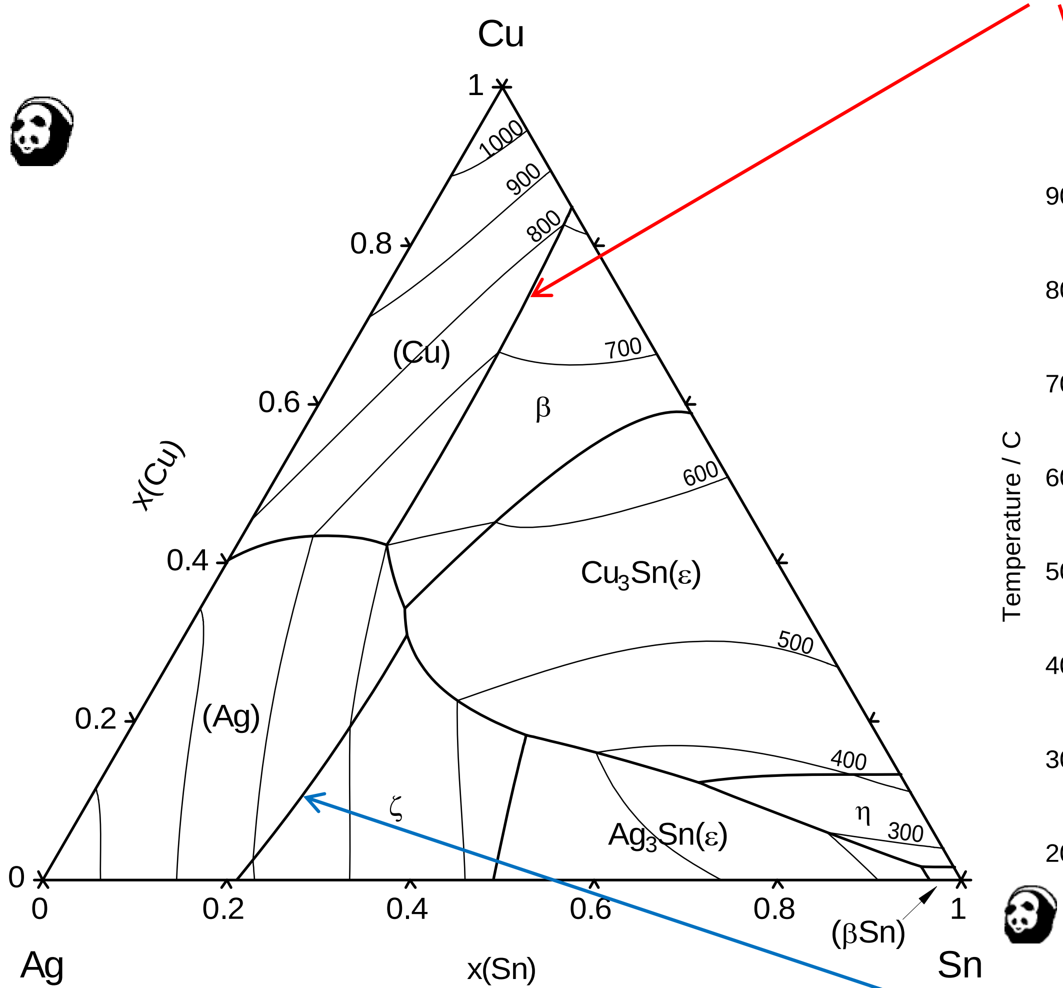
Miscibility gap between Cu_6Sn_5 and Ni_3Sn_2

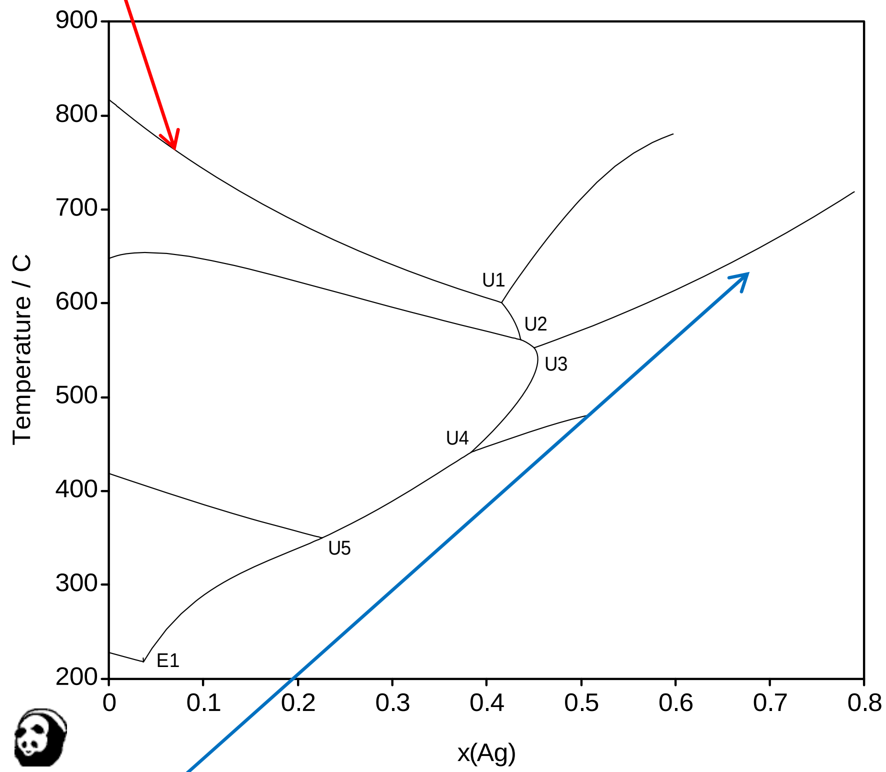


I = Ni_3Sn LT + τ1 + Ni_3Sn_2 HT	IV = Ni_3Sn_2 HT + ζ + (Cu,Ni)
II = τ1 + γ + Ni_3Sn_2 HT	V = Cu_6Sn_5 HT + Ni_3Sn_2 + ζ
III = Ni_3Sn_2 HT + γ + (Cu,Ni)	VI = Cu_6Sn_5 HT + ζ + ε

Applications

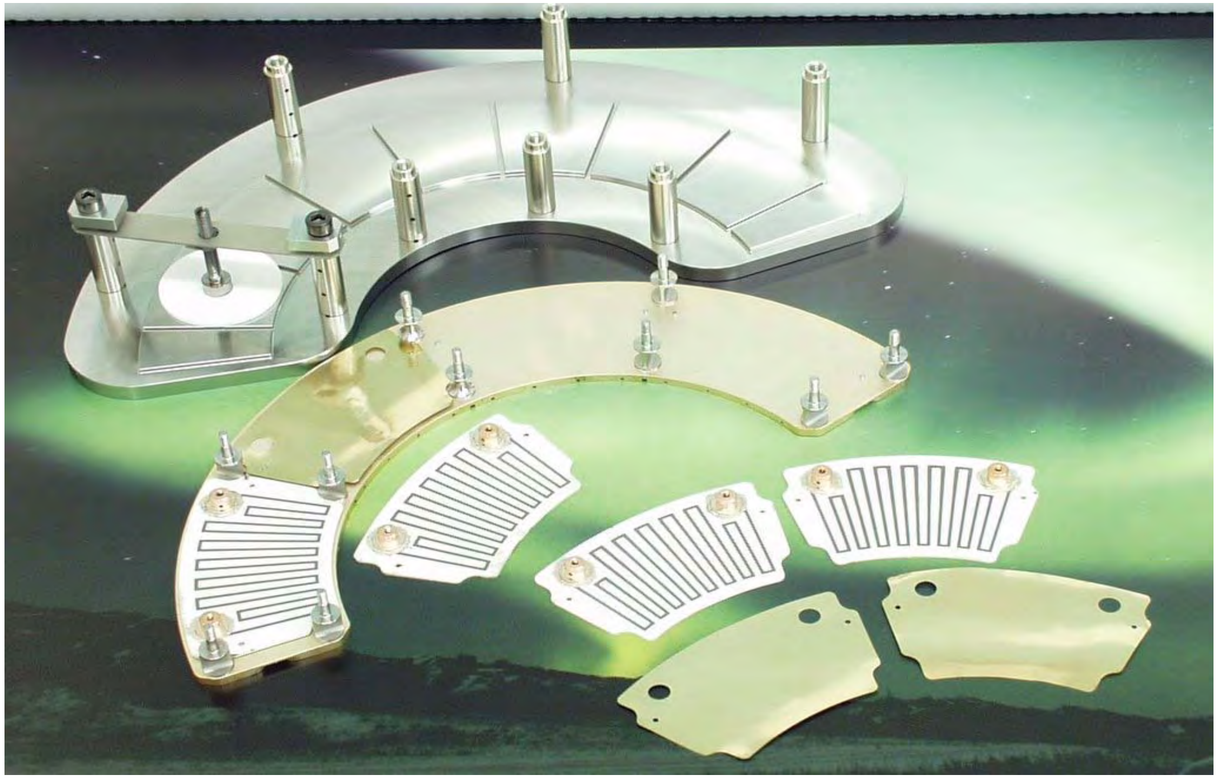
Liquidus projection for solders





Application - Au-Ge

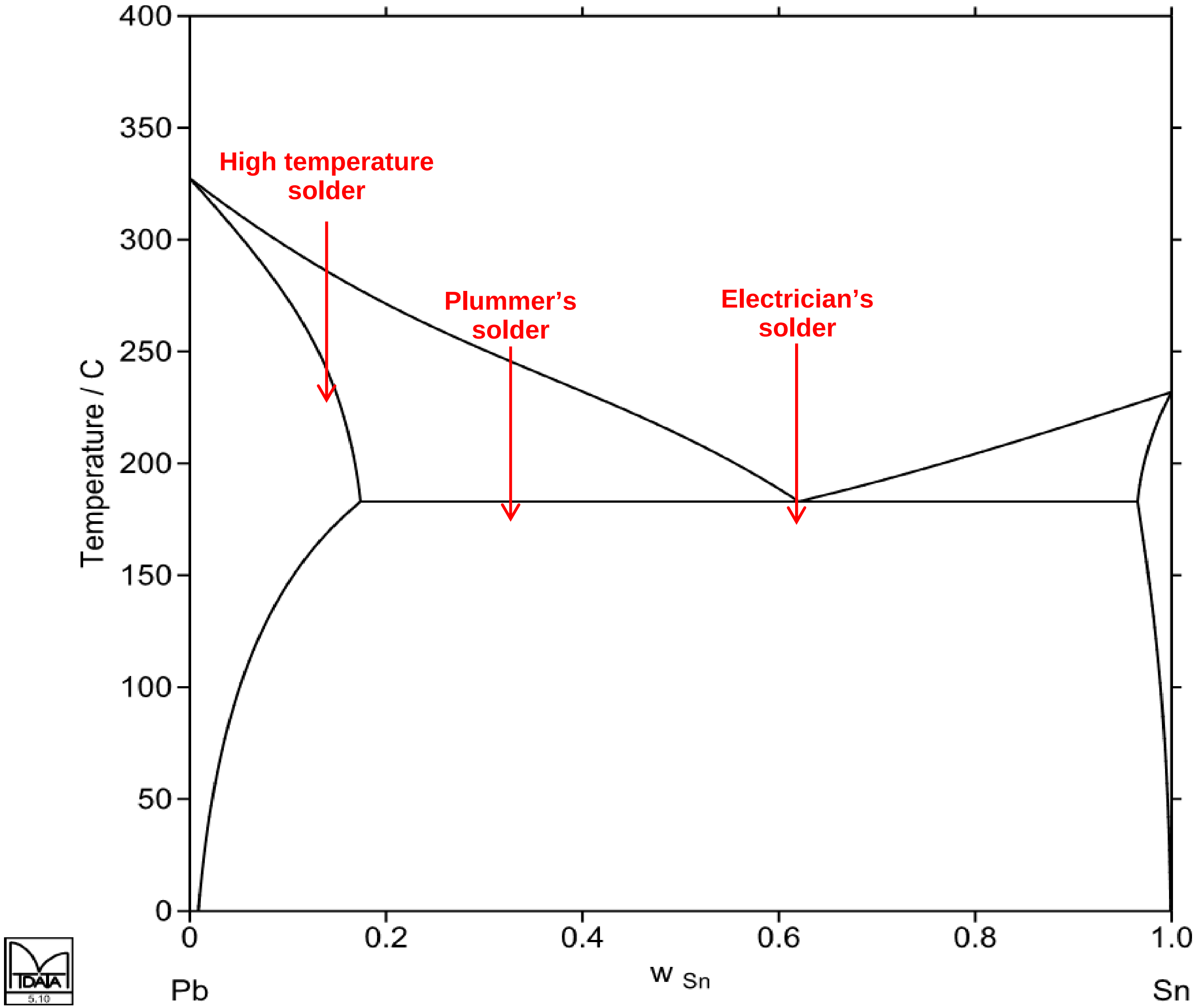
Heated conversion surface assemblies for ESA / JAXA Mission BepiColombo to Mercury (Launch 2014)



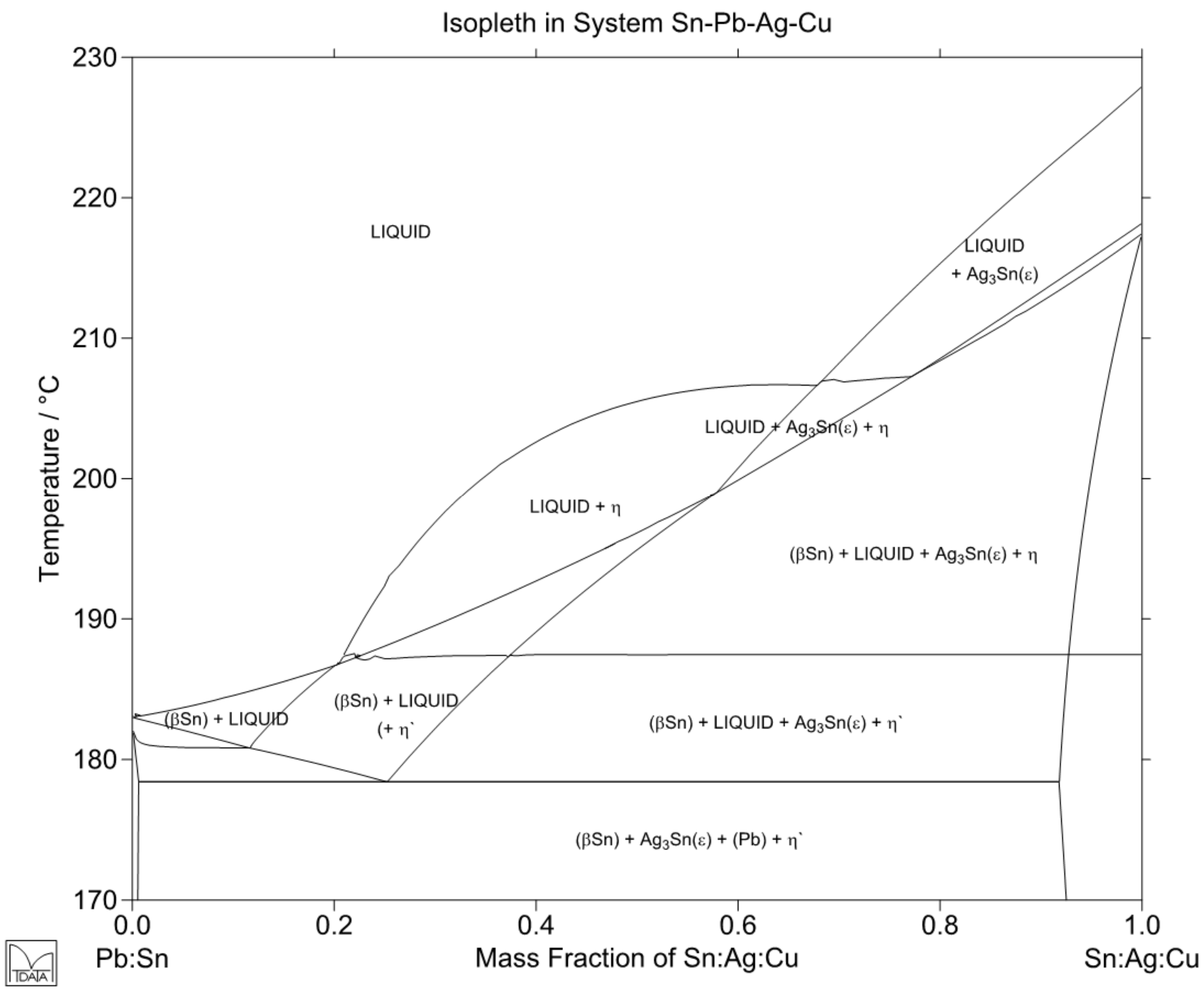
Christian Leinenbach,
EMPA, Switzerland

Investigating the reworking old solder joints

Phase Diagram for the Lead-Tin system



Repair: Mixing electrician's solder with lead free solder



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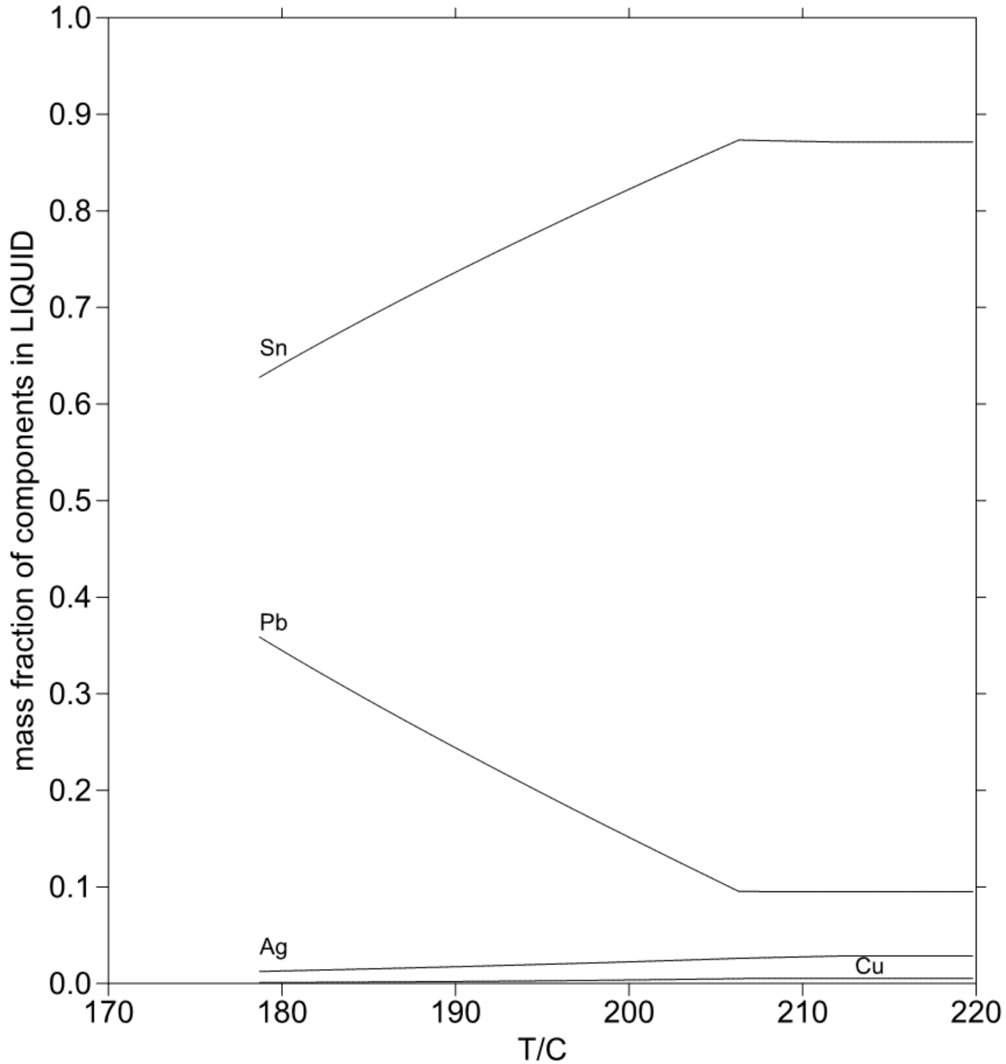
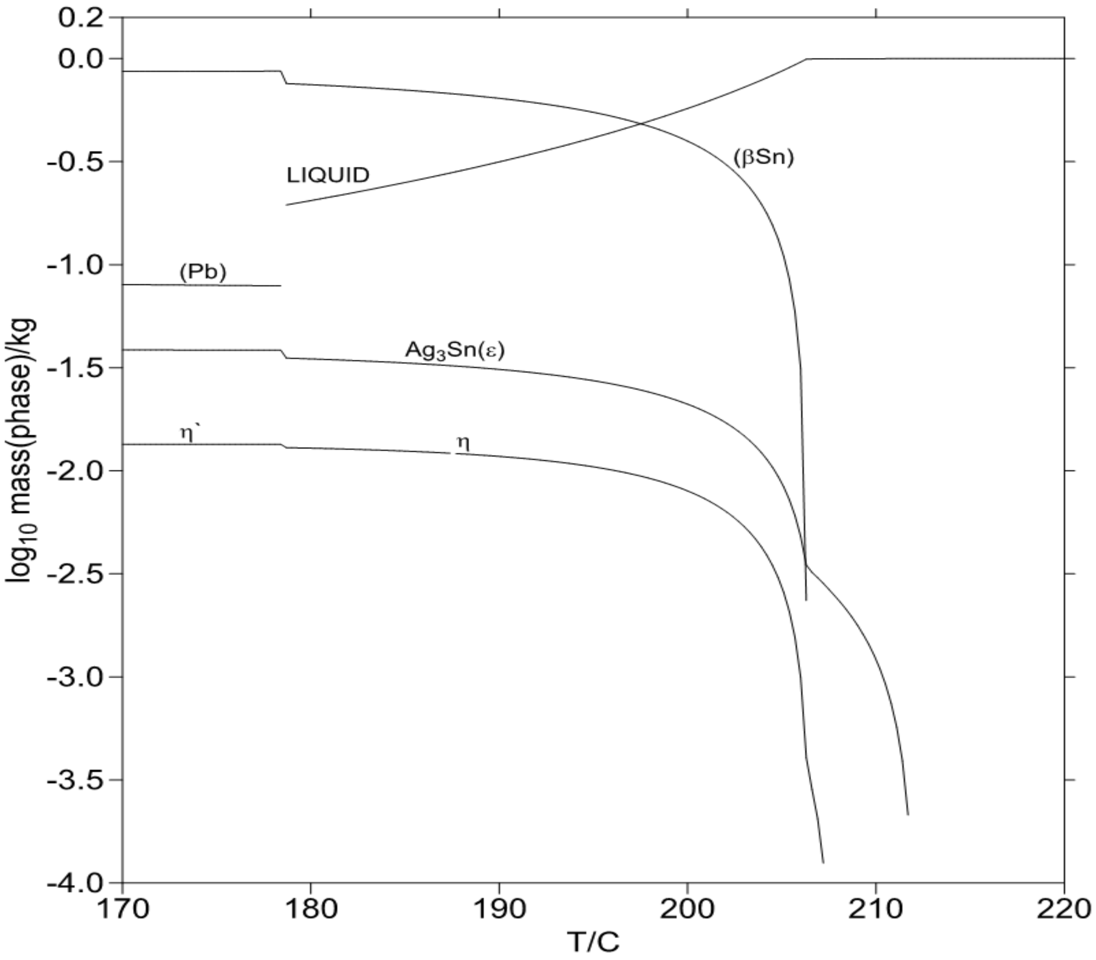
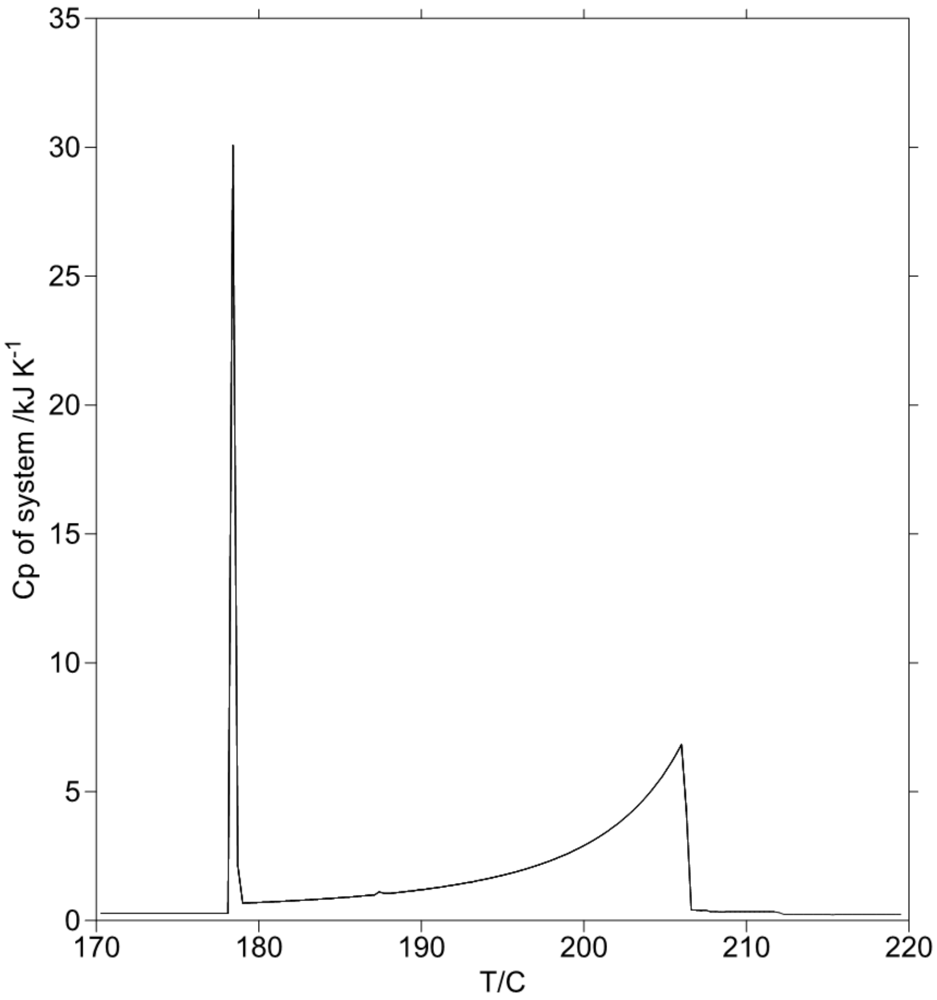
Liquid phase composition: cooling of a mixture of a lead-free solder and a Pb-Sn "electrician's solder"

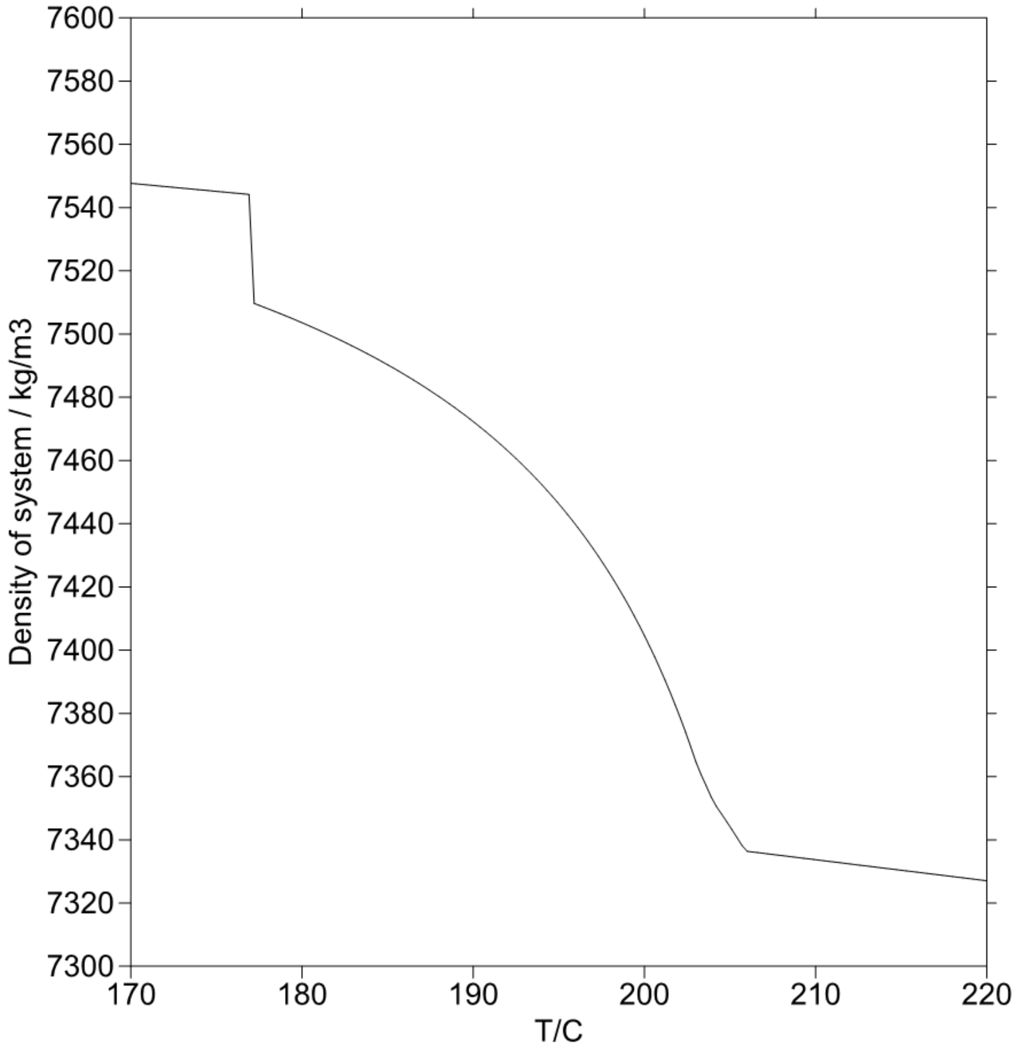


Plot of mass of phases with variation of temperature

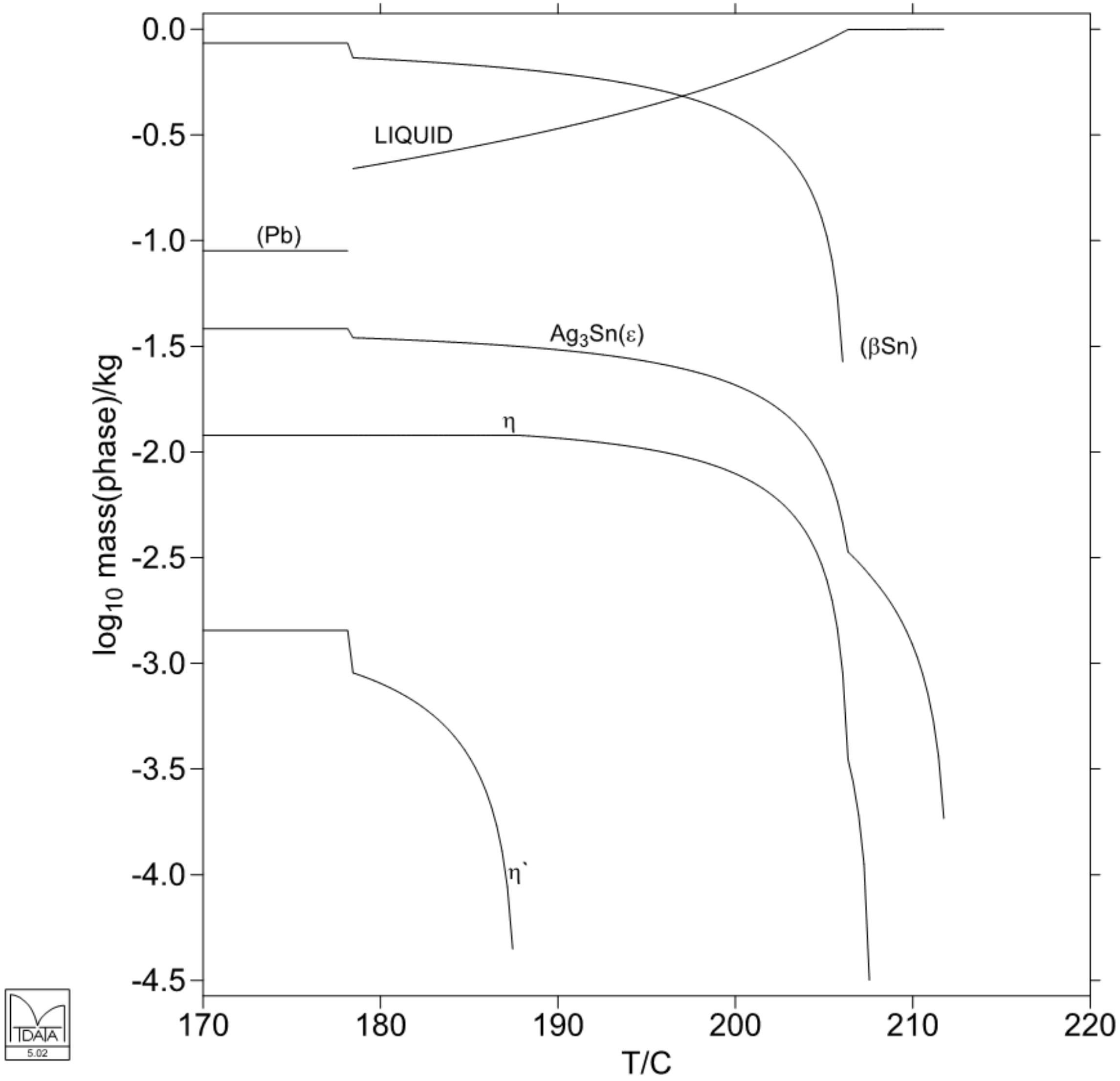


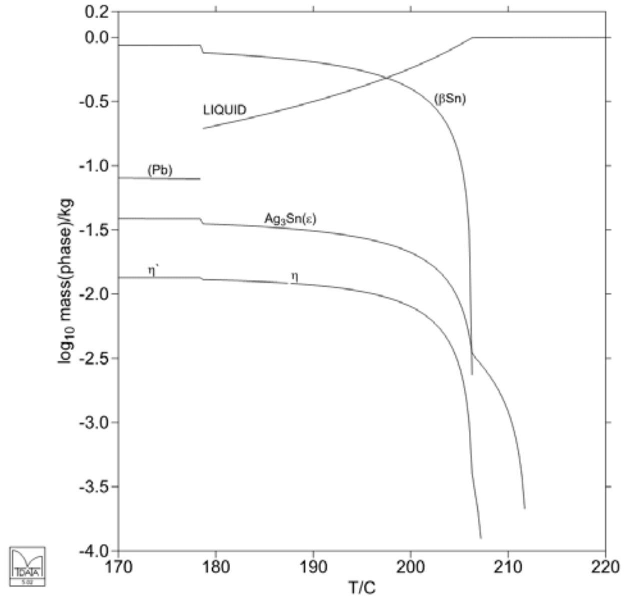
Calculated heat capacity and volume change



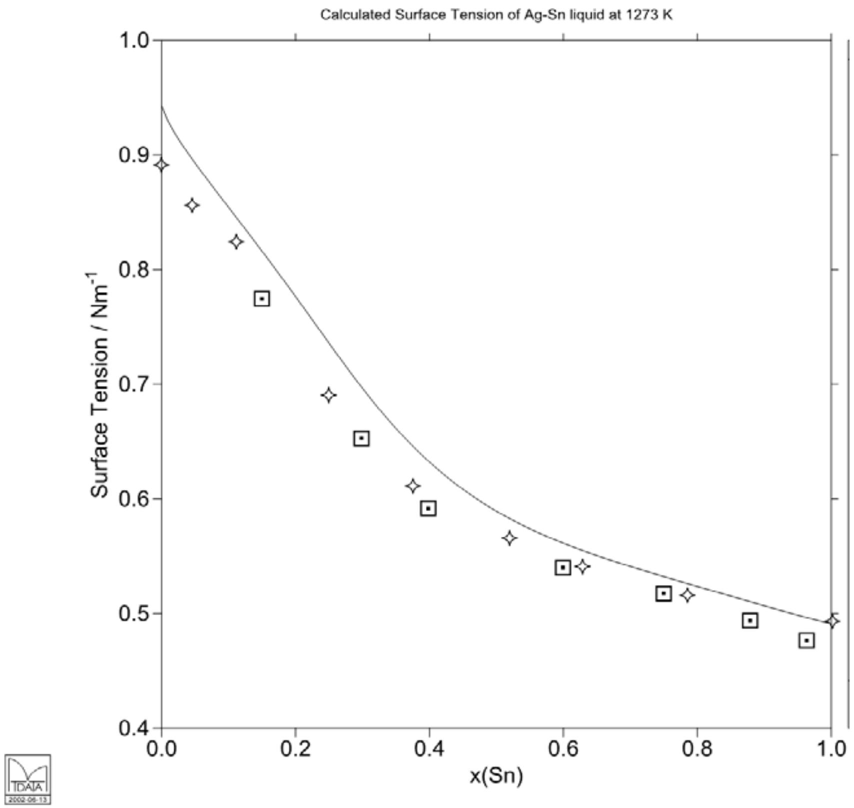


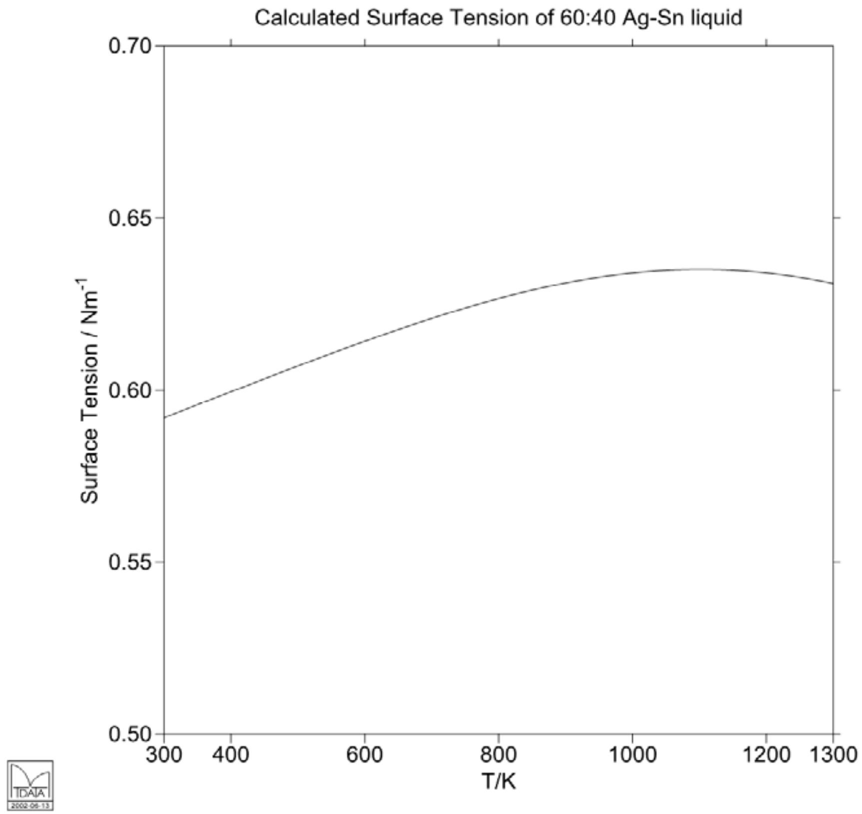
Scheil model of solidification



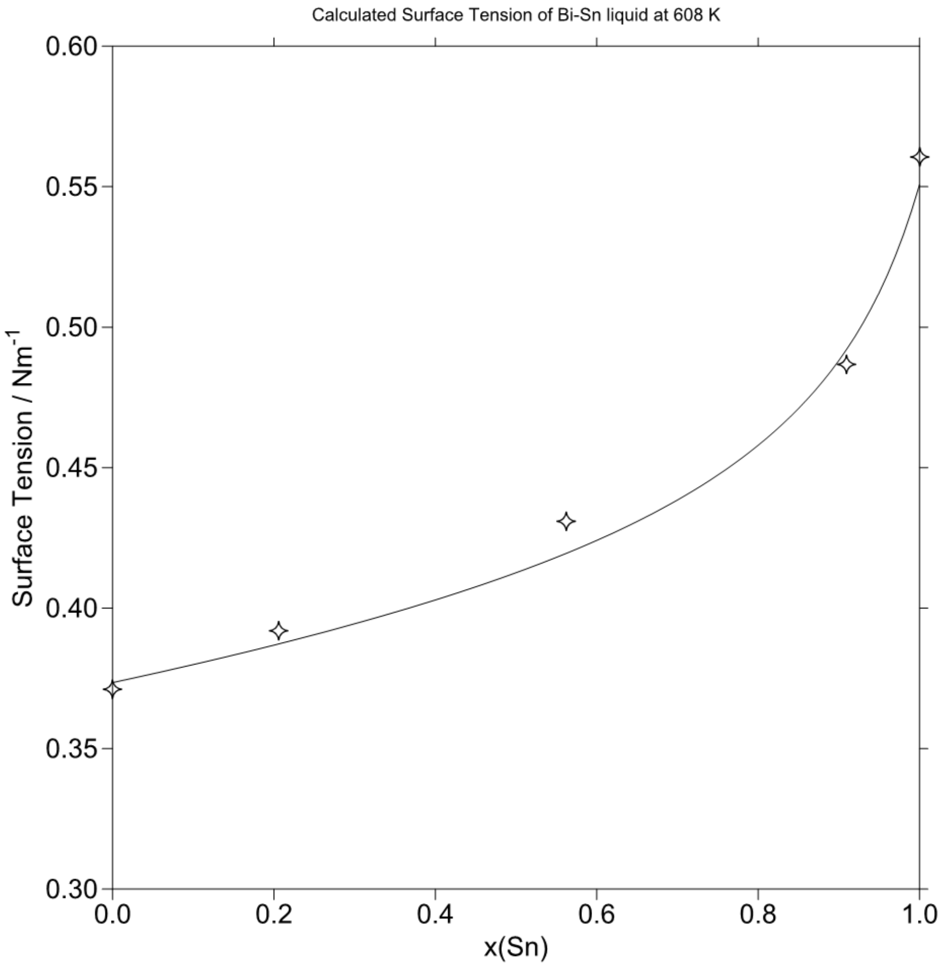


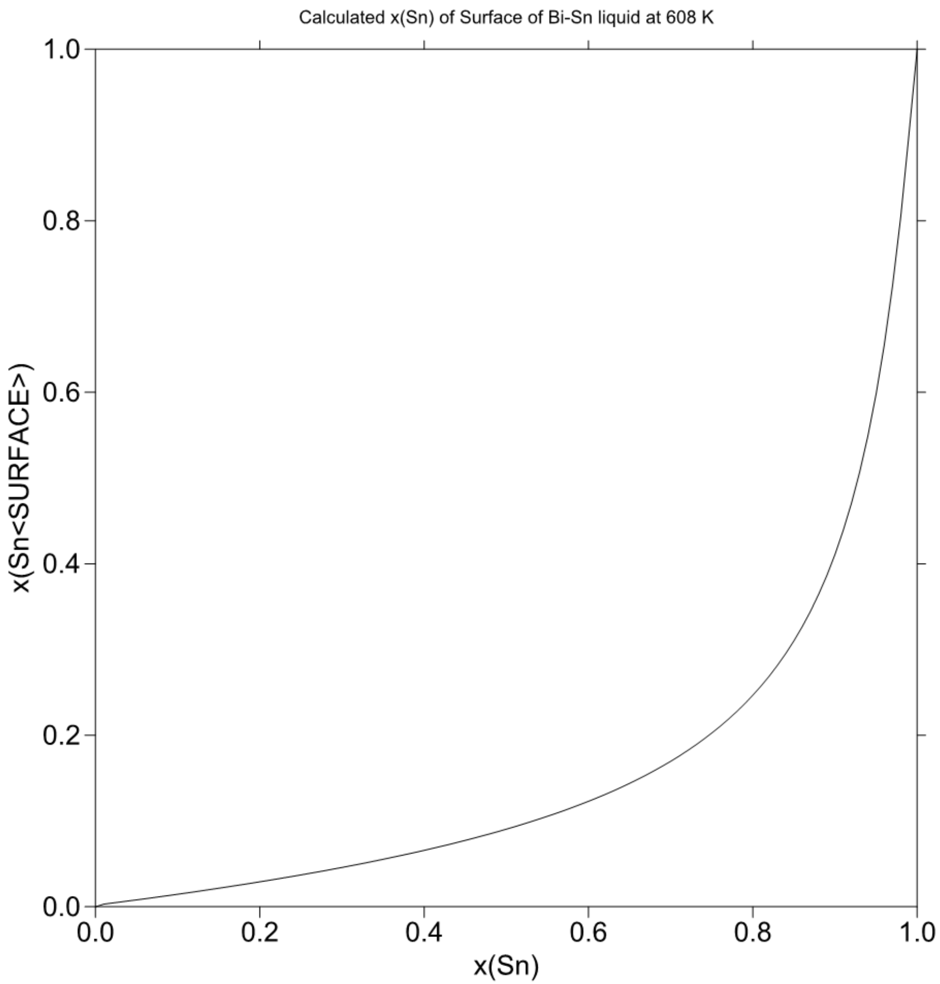
Other properties





Calculated surface tension and surface composition of Bi-Sn liquid





Final remarks

- Brief overview of European projects of solders
- What we have been trying to achieve
- Development and scope of thermodynamic databases
- Modelling issues
- Applications

Acknowledgements

- Aleš Kroupa (Institute of Physics of Materials, AS CR, Brno, Czech Republic)
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Thanks !