



**HAL**  
open science

## New comments on the Melting Entropy of Binary Eutectic Alloys without solid state solubility

Pierre Guiraldenq

► **To cite this version:**

Pierre Guiraldenq. New comments on the Melting Entropy of Binary Eutectic Alloys without solid state solubility. 2023. hal-04032265v3

**HAL Id: hal-04032265**

**<https://ec-lyon.hal.science/hal-04032265v3>**

Preprint submitted on 15 Nov 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

**New comments on the Melting Entropy  
of Binary Eutectic Alloys without solid state solubility**

**Pierre Guiraldenq \***

**Summary**

A new approach is given for the solid - liquid transition at the melting temperature for a family of well known binary eutectic alloys, problem which has been introduced in a preceding paper in 2020.

In a first time, a mechanism is described for the beginning of the melting process, with the role played by the interfaces between the two lattices. A second question concerns the vibration frequencies of atoms at that time for the two components in relation with the self diffusion constants. At the end, it is proposed an order-disorder model by damped oscillations of the entropy before the final stabilized amorphous liquid state.

**KEYWORDS :** eutectic transition, melting entropy, diffusion in the solid state, interfaces, amorphous phases, vibration frequencies.

**\* Emeritus Professor and past director of the Physical Metallurgy and Materials Science Department at the Ecole Centrale de Lyon (University of Lyon), France**

Contact : < [pierre.guiraldenq@orange.fr](mailto:pierre.guiraldenq@orange.fr) >

## 1 A RECALL ON THE PRECEEDING RESULTS :

In a previous paper (1), we have focused on a singularity about a small group of binary eutectic alloys (without solid state solubility) and for which the solid-liquid transformation at the eutectic temperature is characterized by an excess of entropy, compared to other thermodynamic systems (at the atmospheric pressure).

This small group contains nine binary diagrams ;

**Si - Au, Ge-Au, B-Pt, Ge-Al, As-Pb, Ge-Ag, Cd-Bi, Si-Ag, Si-Be**

which corresponds to a simple binary semi-conductor - metal family.

For this family, it has been noted a linear relation between an entropy excess during the melting process,  $\Delta SE$ , with a specific parameter taking in account the self diffusion properties of each component ( $m_1, m_2$ ) by the cumulative ratio of the eutectic temperature  $TE$  compared with the two melting temperatures ( $T_{m1}, T_{m2}$ ) according the relation ;

$$\Delta SE \propto ( TE / T_{m1} + TE / T_{m2} )$$

The Figure 1 shows a linear relationship for this binary alloys family seen before, with a slope which value is  $3 k_B N_A$ , with  $k_B$  the Boltzmann Constant and  $N_A$  the Avogadro Number. Other results with a very low level for  $\Delta S E$  are not taken into account here (Ag - Bi, Al - Sn, Be - Al, etc).

We note with surprise the same property defined a very long time ago by Albert Einstein for the solid state heat capacity corresponding to one simple perfect solid, in which all the atoms have at the end the same vibration frequency (2) (3). The problem is presently clearly different because it concerns, at the same time, two solid phases in equilibrium and in contact, with the classical lamellar eutectic structure giving at the end only one liquid phase, at the same temperature  $TE$ , like a pure metal. To obtain an analysis of this singular state, we have considered two complementary approaches : the first one by a structural analysis at the interfaces between the two components and, in a second way, by a quantitative description of the vibration frequencies calculated with the self diffusion coefficients in the solid state.

## 2 A STRUCTURAL REGARD TO THE EUTECTIC TRANSITION AT A NANOSCOPIC SCALE :

We have described before in (1) the role played by the interfaces between two lamellar phases as simple diffusion couples : We know that several diffusion processes may be present and in which the interfacial diffusion process is preponderant when the ratio  $T_{\text{Eutectic}} / T_m$  is low ( $T_E / T_{m1}$  and  $T_E / T_{m2}$  under 0,5) and, on the contrary, in relation with a bulk diffusion when the ratio  $T_E / T_m$  is larger than 0,6-0,7.

At the beginning and at a very low temperature, before the heating process to the melting temperature  $T_E$ , and taking into account the crystallographic properties of each element, we can consider possible crystallographic coincidences sites between the two systems, as described a long time ago by Aust and Chalmers (4), Smith (5) in 1951, then later by Spaepen in 1975 to describe the liquid transition with an amorphous phase (6).

In a first time, applied to the eutectic Si-Au system, the figure 2 gives a possible equilibrium coincidence sites, taking for instance the same simple (100) plane and the same axis  $\langle 100 \rangle$ , with the crystallographic parameters for each element.

By a rotation of  $20^\circ$  around one axis  $\langle 001 \rangle$  for the Au lattice, it appears for example, at the interface, coincidence sites for Au(F.C.C) and Si (D.C.) every eight atomic positions, the other places being with possible local or other disturbing defects (dislocations, etc)

For very high interfacial energies which characterize the diffusion process, with an increasing temperature and new atomic configurations, we can imagine a progressive structural instability like in Figure 3. The new transitory medium, presented here, like an amorphous zone, should be the progressive evolution toward the liquid state from the initial quasi- ordered structure between the two lamellar phases, giving so an higher transitory entropy compared to the self melting entropy alone.

### 3 ANALYSIS OF THE ATOMIC VIBRATIONS WITH THE DIFFUSION CONSTANTS IN THE SOLID STATE

As said before in (1), the atomic diffusion processes are defined for each element in a binary system by Arrhenius laws giving the diffusion coefficients in the bulk, or in the grain boundaries and interfaces at lower temperatures.

In the present case, we consider only the bulk diffusion coefficients through the Arrhenius law because this mechanism is always present at the same time in the transverse directions of the interfaces at medium temperatures ( $T_E / T_m$  higher than 0.5)

The literature gives a large panel of results obtained with radiotracers or other physical methods, giving the frequency factor  $D_0$  by the well known relation :

$$D_0 = a^2 \nu \exp(-\Delta S/k) \quad \text{equ.}$$

1

with  $k = k$  Boltzmann

$\nu =$  vibration frequency

and "a" the lattice parameter taken at low temperature

(for F.C.C., C.C. and D.C. cubic structures)

In the present case, the entropy which characterizes all the defects present during the transition at  $T_E$ , is the excess of entropy  $\Delta S_E$  which has been calculated in the preceding paper at the melting temperature of the eutectic alloys with this singular property (Figure 1).

So, taking the values of the frequency factor  $D_0$  and the crystal parameters "a" (taken constant at low temperature), we can define an average frequency " $\nu_E$ " for each element corresponding at the end to the solid-liquid transition. We have noted that the two atomic concentrations for CE (with  $CE = C_1 + C_2$ ) at  $T_E$  have no importance at this level because this factor disappears at the atomic scale for the two elements without solubility (each element has the same concentration (100 at. per cent) on each side of the interfaces at low temperature, before heating to  $T_E$ ).

So, we have taken only four typical diagrams covering high and low values for  $\Delta S E$  (with cubic structures and with well defined  $D_0$  values)

**Si - Au      Si - Ag      Ge - Au      Ge - Ag**

For each case, the best  $D_0$  experimental values have been chosen in the literature (7) (8) and the lattice parameters from the classical Charles S. Barrett book (9) :

<b>Au</b>	<b><math>D_0 = 0.09 \cdot 10^{-4} \text{ (m}^2 / \text{sec)}</math></b>	<b>a = 0,4078</b>	<b>nm</b>
<b>Ag</b>	<b><math>D_0 = 0.44 \cdot 10^{-4}</math></b>	<b>"</b>	<b>a = 0,4085 "</b>
<b>Si</b>	<b><math>D_0 = 2 \cdot 10^{-1}</math></b>	<b>"</b>	<b>a = 0,5422 "</b>
<b>Ge</b>	<b><math>D_0 = 7.8 \cdot 10^{-4}</math></b>	<b>"</b>	<b>a = 0,5658 "</b>

The table gives below the frequencies  $\nu E$  obtained by this way from equ.1

<b>Alloy</b>	<b>T E ( K )</b>	<b>TE/Tm1 + TE/Tm2</b>	<b><math>\nu E</math> ( Hz )</b>	<b><math>\nu_1/\nu_2 \approx</math></b>
<b>Si</b>	<b>643</b>	<b>0,85</b>	<b><math>2.9 \cdot 10^{+16}</math></b>	<b>10+4</b>
<b>Au</b>	<b>"</b>	<b>"</b>	<b><math>2.3 \cdot 10^{+12}</math></b>	
<b>Si</b>	<b>1103</b>	<b>1,54</b>	<b><math>2.9 \cdot 10^{+16}</math></b>	<b>10+3</b>
<b>Ag</b>	<b>"</b>	<b>"</b>	<b><math>1.1 \cdot 10^{+13}</math></b>	
<b>Ge</b>	<b>629</b>	<b>0,98</b>	<b><math>1 \cdot 10^{+14}</math></b>	<b>10+2</b>
<b>Au</b>	<b>"</b>	<b>"</b>	<b><math>2.3 \cdot 10^{+12}</math></b>	
<b>Ge</b>	<b>924</b>	<b>1,5</b>	<b><math>1 \cdot 10^{+14}</math></b>	<b>10+1</b>
<b>Ag</b>	<b>"</b>	<b>"</b>	<b><math>1.1 \cdot 10^{+13}</math></b>	

Between these different binary alloys, we note a decreasing ratio of the vibration frequencies which values are in coherence with many other physical properties. It is certainly the expression of different atomic interactions during the solid-liquid transition at TE between the structure of a semi-conductor (Si or Ge) with a classical noble metal (Au or Ag). These same components have been a long time ago studied at an atomic level for electronic devices (10) and for the vibration frequencies in the crystalline or amorphous states by P. Dean (11) and A.T. Willis and A.W. Prior (12).

In the present case, the vibration frequencies  $\nu E$  have been obtained only in relation with the diffusion mechanisms and it should be interesting, with new other methods, like Laser Spectroscopy, to obtain in situ confirmation of these results. The other cases, seen in the Figure 1, should be also discussed, but with some difficulties according their different crystalline structures (B, Be, Sn, As, Bi, Th) and the best rigorous values obtained for the self diffusion constants  $D_0$ , as said before.

At the end and for the progressive evolution of the micro structure of such eutectic alloys to the amorphous liquid state at TE, it is possible to imagine a damped oscillations process, starting from the interfaces toward the bulk, like in the figure 3 with new transitory configurations. A such decreasing evolution of the ordered duplex lamellar structure should be so described by a Fourier series model (13) for the entropy  $\Delta S E$  before the final liquid eutectic state (Figure 4).

#### **4 FINAL CONCLUSION :**

Using the simple thermodynamic concepts, a new analysis has been suggested with a singular family of binary alloys, characterized by an insolubility in the solid state.

It has been noted a set of such alloys which match this property with a singular entropy corresponding to the melting temperature in relation with a factor  $3kN$ , which has been formerly taken as a reference to define the upper solid state heat capacity.

This historical review inside the Materials Science chapter, particularly with only the self diffusion constants to define the atomic vibrations, has shed some light at a nano scale level of a singular new alloys family concerning the order-disorder phenomena during the solid-liquid transitions.

**Conflicts of interest :** the author declare no conflict of interest

**ACKNOWLEDGEMENTS :** to Dr Jean Marie Dubois, Emeritus Director of CNRS at the Institut Jean Lamour (UMR CNRS 7198) - Nancy University - for his encouragements, discussion in detail and corrections.

### FINAL IMPORTANT REMARK

The Al-Be eutectic system has been taken here as an example with a very small  $\Delta S$  E value (near zero).

As said before, taking into account the crystallographic parameters and the bulk self diffusion constants  $D_0$  given by the literature (9) (14) :

<b>Al (F.C.C.)</b>	<b>a = 0. 4049 nm</b>	<b><math>D_0 = 1.71 \cdot 10^{-4} \text{ (m}^2 \text{ / sec)}</math> (14)</b>
<b>Be (C.P.H.)</b>	<b>a = 0. 2285 nm //</b>	<b><math>D_0 = 0.62 \cdot 10^{-4} \text{ (m}^2 \text{ / sec)}</math> // (c axis)</b>
	<b>c = 0. 3584 nm <math>\perp</math></b>	<b><math>D_0 = 0.52 \cdot 10^{-4} \text{ (m}^2 \text{ / sec)}</math> <math>\perp</math> (basic plane)</b>

For Be, the self-diffusion results have been obtained with single crystals along two directions (along the // (c axis), and the  $\perp$  (basic plane) (14)).

So, the vibration frequencies obtained with the frequency factors  $D_0$  are for each element :

$$\begin{aligned} \nu (\text{Al}) &= 4.46 \cdot 10^{+13} \text{ Hz} & \nu (\text{Be}) &= 5.08 \cdot 10^{+13} \text{ Hz // (c axis)} \\ & & \nu (\text{Be}) &= 1.73 \cdot 10^{+13} \text{ Hz } \perp \text{ (basic plane)} \end{aligned}$$

Considering the medium value of  $\nu$  (Be) in the bulk as a first approximation, that is  $3.4 \cdot 10^{+13}$  Hz, the ratio  $\nu$  (Be) /  $\nu$  (Al), or the reverse ratio  $\nu$  (Al) /  $\nu$  (Be), is finally near the value : 1, value which is very lower than the all other results for the cases studied previously in § 3 (page 4). This means, when  $\Delta S$  E = 0, that the vibration frequency of the two elements is probably the same near the interfaces



## 8

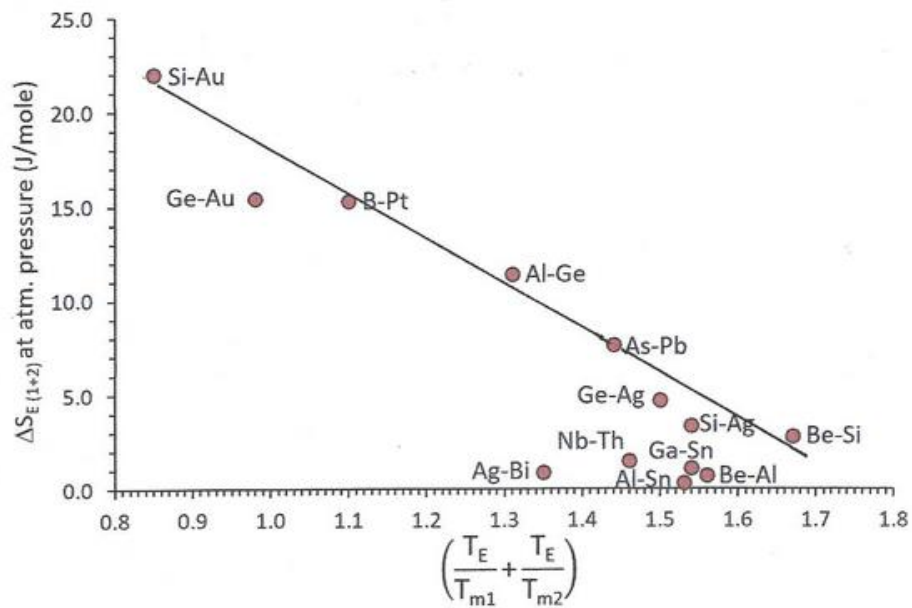
during the final solid  $\rightarrow$  liquid transformation, like for a pure metal in the grain boundaries at its melting temperature and according the Gibbs phases rule.

The other cases seen before, with high transitory entropy and with high difference between the frequencies (the best case is Au-Si), are explained by quasi amorphous disordered structures during the melting process.

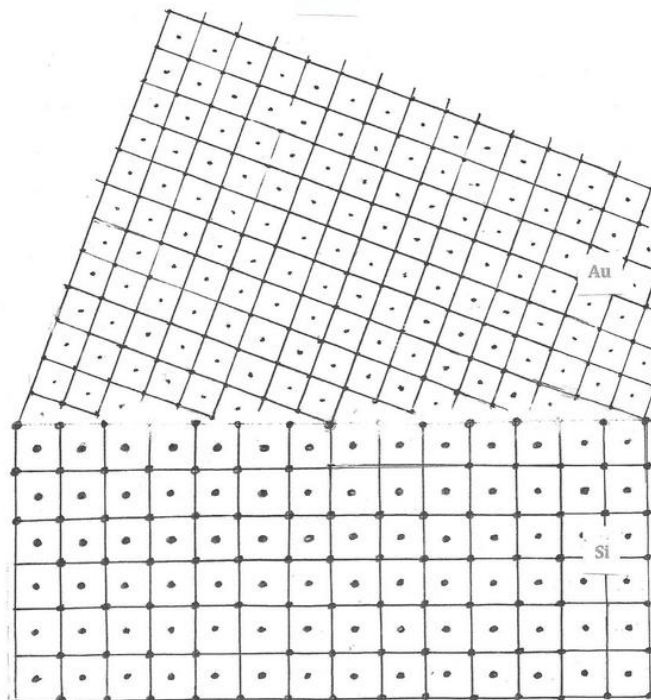
**REFERENCES :**

- 1** Guiraldenq P. A new approach to the solid-liquid transition for simple binary eutectic systems in relation to the melting entropy and the periodic Table : Research Gate June  
DOI : 10.13140/RG.2.235888.99844 (2020)
- 2** Einstein A. L'état actuel du problème des chaleurs spécifiques ; La théorie du rayonnement et les quantas - Rapport et discussions de la réunion tenue à Bruxelles 30 oct.-3 nov. 1911 Gauthier-Villard Paris 407- 450 (1912)
- 3** Fast J.D. Entropy Philips Technical Librairy Eindhoven. (1960)  
traduit en français par E.J. Clément Dunod Paris 78-80 (1961)
- 4** Aust R.T., Chalmers B. Energy and structure of grain boundaries, Metal Interface ASM, Detroit, oct. 13 to 19 – 1951 – Cleveland. Ed ASM, 153-178 (1952)
- 5** Smith C.S. Grain shapes and other metallurgical applications of topology Idem ASM, 65-113 (1952)
- 6** Spaepen F. A structural model for the solid-liquid interface in monoatomic systems Acta Metallurgica 23 june, 729 -743 (1975)
- 7** Philibert J. Atom movements Diffusion and mass transport in solids Les Editions de Physique Les Ulis, 107, 115, 116, 121 (1991)
- 8** Boltaks B. Diffusion et défauts ponctuels dans les semi- conducteurs Ed. Mir Moscou. Traduit du russe par S. Medvedev, 145, 181 (1977)
- 9** Barrett C.S. Structure of metals Mc Graw Hill N.Y.,646 - 649 (1952)  
traduit en français par C. Leymonie Dunud Paris, 606-609 (1957)
- 10** Brillson L. The structure and properties of metal –semiconductors interfaces Surface Science reports nov. 123- 326 (1982)
- 11** Dean P. Atomic vibrations in Solids J. Inst. Maths Applies 3, 98-165 (1967)
- 12** Willis B.T. Pryor A.W. Thermal vibrations in Crystallography. Ed. Cambridge University Press (1975).
- 13** Angot B. Compléments de Mathématiques à l'usage des ingénieurs de l' Electrotechnique et des Télécommunications. Ed. Revue d'Optique Collection Technique du CENT Paris, 63- 65 (1952).
- 14** Lundy T.S., Murdock J.F. (Al) and Dupuy J.M., Mathia J., Adda Y. (Be)References in Adda Y., Philibert J. La diffusion dans les solides Tome II Presses Universitaires de France Paris, 1129 and 1132 (1966).

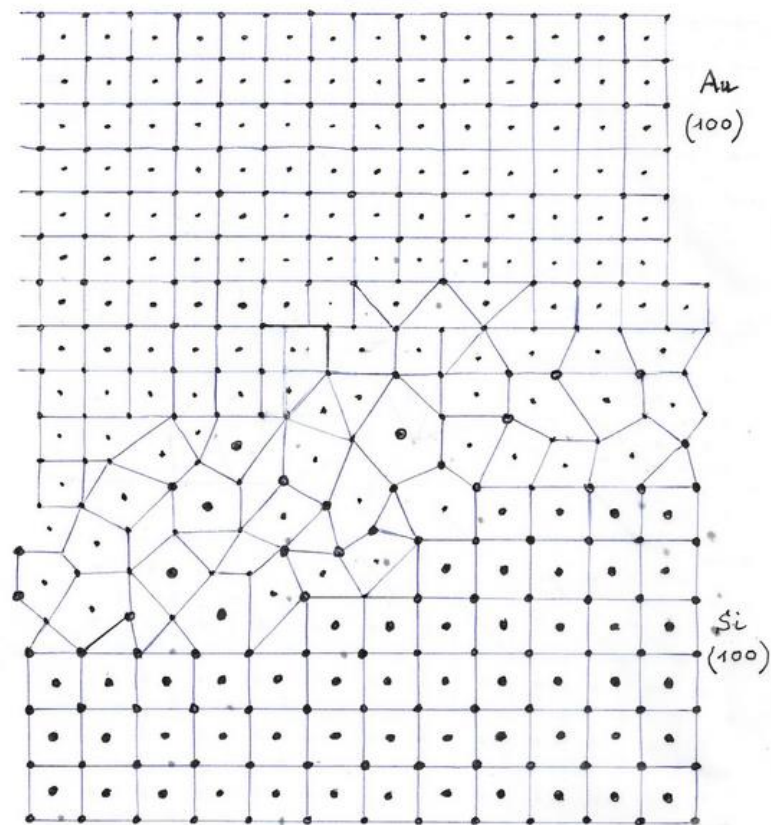
FIGURES 1 to 4 (pages 9 to 10)



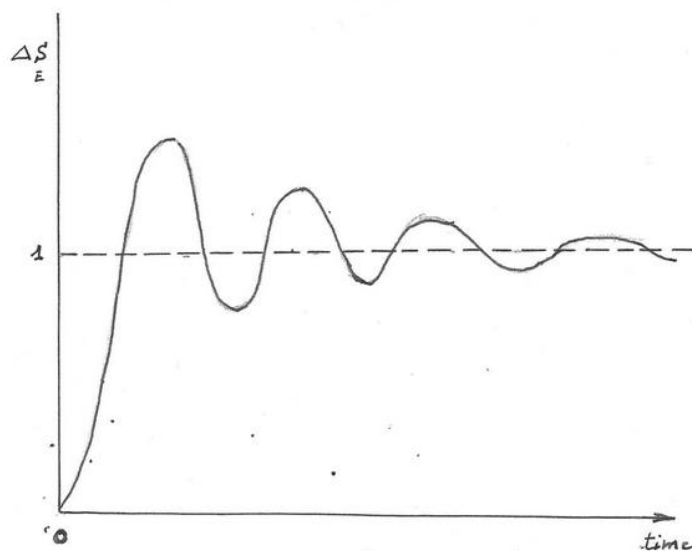
**Figure 1** : Recall for the increasing entropy obtained at TE during the transformation solid-liquid as a function of the parameter  $\left(\frac{T_E}{T_{m1}} + \frac{T_E}{T_{m2}}\right)$  for binary eutectic alloys without solid state solubility (1)



**Figure 2** : Coincidence sites at the interface between the two elements Si and Au in the same plane (100) and a rotation of 20 degrees for Au lattice around an axis  $\langle 001 \rangle$  (parameters ref. (9))



**Figure 3 :** The possible first evolution of the interface between the two lattices of Au and Si, for the same plane (100) without rotation and with several local distortions of the two lattices under the influence of vibration frequencies and short range diffusion at TE.



**Figure 4 :** Evolution of the entropy excess at TE, growing from the interfacial zones by a damping oscillations process during the progressive transformation of the eutectic structure to the final amorphous liquid state.