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TINY CRYSTALS SURVIVING ABOVE THE MELTING TEMPERATURE AND ACTING AS GROWTH NUCLEI OF SUPERCONDUCTOR MICROSTRUCTURE

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Abstract: Magnetic field texturing has shown the possible existence of intrinsic solid nuclei surviving above the melting temperature T_m and governing the solidification. Tiny crystals could survive above T_m and act as growth nuclei with undercooling ratios $\theta = (T - T_m)/T_m$ larger than the theoretical value $\theta \leq 2/3$ if a negative supplementary volume energy α_{1ls} is missing in the Gibbs free energy change associated to the formation of a critical cluster. A double layer of opposite charges could create the solid-liquid interface electrostatic energy α_{1ls} . The observed values θ_1 and the dimensionless surface energies α_{1ls} calculated for 38 liquid elements assumed as being homogeneous are used to determine $-\alpha_v(\theta)$ of all liquid elements containing intrinsic solid nuclei. The α_v values at $T = T_m$ are equal to 21.7% of the fusion heat per volume unit. The dimensionless surface energy α_{2ls} multiplied by the fusion entropies are the same for all elements. After melting these tiny crystals around $T_{m2} = 1.20T_m$, all the undercooling ratios could tend to $-2/3$.

Introduction

Large undercooling ratios $\theta_1 = (T - T_m)/T_m < 0$ have been observed on many liquid elements after an overheating $\theta = \theta_s$ sufficiently large to dissolve foreign particles suspended in the melt which could act as heterogeneous nuclei [1, 2]. Contactless electromagnetic or electrostatic processing, droplet free-fall tower and dispersion techniques have produced θ_1 values smaller than 0.3 except for elements having a low melting temperature T_m : Hg- ($T_m = 232$ K. $\theta_1 = -0.38$), Ga- ($T_m = 303$ K. $\theta_1 = -0.58$), Sn- ($T_m = 520$ K. $\theta_1 = -0.37$), Bi- ($T_m = 544$ K. $\theta_1 = -0.42$), Te- ($T_m = 723$ K. $\theta_1 = -0.33$) [see [1] and references therein]. These elements are easily overheated above T_m ; in particular, the overheating ratios applied to mercury and gallium were larger than 0.29. In the case of a free-fall tower furnace, the applied overheating ratios are smaller because a hanging droplet technique is often used.

The theoretical frequency J of crystal nucleus formation per volume unit and per second in undercooled homogeneous melts [3] is varying with θ , the fusion entropy ΔS_m , the dimensionless surface energy α_{1ls} and K_v a frequency per m^3 and per second of the order of $10^{40 \pm 1}$ which is slowly varying with temperature and elements [1]. K_v includes a coefficient $\exp(-Q/k_B T)$ related to atom diffusion through the liquid-solid interface [4]. The diffusion coefficient from the liquid to the solid is weakly varying through elements while Q from the solid to the liquid is strongly varying. The droplet volume v and the nucleation time t are determined from the experiments. J is given by (1) for a homogeneous liquid and by (2) when larger number of residual nuclei per volume unit are present in the liquid droplets and a time dependence is observed; $\Delta G^*(\theta)$ given in (3) is the critical energy barrier corresponding to the critical radius above which the crystal growth takes place; N_A is the Avogadro number and k_B the Boltzmann constant; the surface energy σ_{1ls} given by (4) is transformed in a volume energy by multiplying it by the mean distance between atoms in the melt; this last quantity is then equal to a fraction α_{1ls} of the fusion heat per volume unit $\Delta H_m/V_m$:

$$\ln J = \ln(K_v) - \frac{\Delta G^*(\theta)}{k_B T} \quad (1)$$

$$\ln(J.v.t) = \ln(K_v.v.t) - \frac{\Delta G^*(\theta)}{k_B T} \quad (2)$$

$$\frac{\Delta G_1^*(\theta)}{k_B T} = \frac{16\pi\Delta S_m\alpha_{1s}^3}{3N_A k_B \theta^2 (1+\theta)} \quad (3)$$

$$\sigma_{1s} \times \left(\frac{V_m}{N_A}\right)^{1/3} = \alpha_{1s} \times \frac{\Delta H_m}{V_m} \quad (4)$$

This classical nucleation model (CNM) [3, 4] does not predict the existence of surviving crystals above T_m ; the critical radius becomes infinite for $\theta=0$ and negative for $\theta>0$; it is also neglecting the free energy of clusters due to stresses arising from volume changes related to the transition solid-liquid [2].

The theoretical frequency J attains a maximum for $\theta=-2/3$. A single crystal grows around a unique critical nucleus when $J.v.t=1$ and $\ln(J.v.t)=0$ [1]. This phenomenon is observed for $\theta=\theta_1$, θ_1 being always larger than $-2/3$ in contradiction with the classical nucleation model. The values θ_1 of 38 elements have been assembled from the literature for $v.t=10^{8\pm1} \text{ m}^3.\text{s}^{-1}$. The dimensionless surface energy α_{1s} is calculated from the knowledge of K_v , ΔS_m and θ_1 . Assuming that the melts are homogeneous because the existence of intrinsic clusters are not possible inside CNM, the undercooling ratio θ of each element is seen as having a minimum for $\theta=\theta_1$ instead of $\theta=-2/3$. Contradictions in this CNM application appear in few cases because values of θ slightly smaller than θ_1 are observed; in particular, gallium has $\theta_1=0.5$ in spite of a minimum value of 0.58 observed for smaller volumes v [5]. The product $\alpha_{1s}^3.\Delta S_m$ is nevertheless determined as being equal to $35.9 \times \theta_1^2(1+\theta_1)$ [6]. The dimensionless surface energy α_{1s} tends to zero with θ_1 suggesting that the surface energy disappears for $\theta=0$ in spite of the fact that θ_1 can be decreased to zero by reducing the overheating temperature. This observation is suggesting that the undercooling could depend on the overheating and that α_{1s} is not the expected dimensionless surface energy. The overheating ratio could have been too small to eliminate surviving crystals.

The existence of microheterogeneities in liquid alloys is now established [7, 8]. A large overheating is necessary to dissolve them and to obtain a homogeneous liquid. These entities are not viewed as being stable. The microheterogeneous state in liquid alloys is attributed to “a long-lived metastable non-equilibrium one with prolonged relaxation time”. As an example, the undercooling ratio of the bulk metallic glass $\text{Ti}_{34}\text{Zr}_{11}\text{Cu}_{47}\text{Ni}_8$ prepared by electrostatic levitation has been studied as a function of the overheating ratio [9]. The undercooling ratio is varying from -0.14 to -0.195 when the overheating ratio increases from 0.172 to 0.258. Nuclei are present in the melt and are governing the solidification.

The undercooling ratio of pure bismuth is not only depending on the overheating rate but also on the overheating period. The authors have suggested the presence of solid bismuth particles progressively melted with time [10].

Processing magnetic materials in a magnetic field is building solids having their elementary grains aligned along an easy-magnetization axis. Melts are containing solid nuclei which can be aligned during solidification in a magnetic field when the applied overheating ratios θ_σ are not larger than a critical value $\theta_c \cong 10^{-3}$ or 10^{-2} [11]. Alignment is very weak when overheating ratios are larger than θ_c . These results are strongly suggesting the possible existence of unmelted crystals of intrinsic nature.

The objective of this paper is to examine the assumption of the existence of intrinsic nuclei which could precipitate the solidification in many melts well above $\theta=-2/3$ by reducing the energy barrier due to the free energy saving related to the previous solidification of surviving crystals. A much better agreement between the experimental results and CNM can be obtained when a negative

contribution $-\varepsilon_v \times 4\pi R^3/3$ is added to the free energy change due to the phase transformation [6, 11]. This energy per volume unit $-\varepsilon_v(\theta_1)$ is determined from α_{1ls} and θ_1 as being equal to 21.7% of the fusion heat per volume unit for $\theta=0$. Its contribution to the new dimensionless surface energy α_{2ls} is small but not negligible because it increases α_{2ls} by 21.7% for $\theta=0$; ε_v decreases with θ^2 down to zero when $\theta \cong -0.63$. This value corresponds to many observations of the disappearance of the free volume for $\theta \cong -0.66$ in amorphous metallic alloys [12].

2- Modifying the classical nucleation-growth model by adding a new contribution $-\varepsilon_v$ per volume unit to the Gibbs free energy change associated to a crystal formation in homogeneous melts

A supplementary contribution $-\varepsilon_v$ per volume unit is expected in many substances because an electron transfer from the solid to the liquid or from the liquid to the solid is equalizing the Fermi energies. An electrostatic interaction between opposite charges carried by two interface layers would correspond to the energy saving associated to this electron transfer. It would be associated to the volume change at the phase transformation. In nonmetallic substances, the change of electronic density at the interface solid-liquid could lead to charged colloids and also induce an electrostatic double layer. There would be Z_m charges carried by each layer separated by a very small distance. In these conditions, the electrostatic energy of a critical radius cluster would be proportional to $e^2 Z_m^2 / R_{2ls}$ and varying as R_{2ls}^3 under the condition that the surface charge density is not dependent on the radius; the charge number Z_m per tiny crystal would increase as R_{2ls}^2 .

The electrostatic contribution $-\varepsilon_v$ is introduced in the free energy change ΔG_{2ls} associated to the transformation as shown in (5):

$$\Delta G_{2ls}(T) = (\Delta G_v - \varepsilon_v) 4\pi \frac{R^3}{3} + 4\pi R^2 \sigma_{2ls} \quad (5)$$

The critical radius R_{2ls} is now defined by (6), σ_{2ls} being the new surface energy, α_{2ls} the new dimensionless surface energy defined by an equation similar to (4); ε_v is defined as a fraction ε_{ls} of the fusion heat per volume unit in (7):

$$R_{2ls}^* = -2 \frac{\sigma_{2ls}}{\Delta G_v - \varepsilon_v} = -2 \frac{\alpha_{2ls}}{\theta - \varepsilon_{ls}} \left(\frac{V_m}{N_A} \right)^{1/3} \quad (6)$$

$$\varepsilon_v = \varepsilon_{ls} \frac{\Delta H_m}{V_m} \quad (7)$$

The critical energy barrier $\Delta G_2^*(\theta)$ is given by (8):

$$\frac{\Delta G_2^*}{k_B T} = \frac{16\pi \Delta S_m \alpha_{2ls}^3}{3N_A k_B (\theta - \varepsilon_{ls})^2 (1 + \theta)} \quad (8)$$

The new nucleation rate J_2 is given by (1) and (2) with $\Delta G^*/k_B T = \Delta G_2^*/k_B T$; its maximum value is obtained for $d \ln J / d\theta = 0$ and

$$\theta_2 = (\varepsilon_{ls} - 2)/3 \quad (9)$$

The value $\theta_2 = -2/3$ is found again for $\varepsilon_{ls} = 0$. This revised model also predicts the presence of tiny crystals surviving in the melt for $\theta < \varepsilon_{ls}(\theta)$ up to their melting temperature T_{m2} . The critical radius R_{2ls} is diverging when θ tends to ε_{ls} i.e. T tending to T_{m2} :

$$T_{m2} = (1 + \varepsilon_{ls}) T_m \quad (10)$$

3- Determination of the electrostatic energy $-\varepsilon_v$ and the new surface energy σ_{2ls} as a function of θ from the undercooling of 38 elements

A first relation (11) between α_{2ls} and ε_{ls} is obtained by combining (1) and (8) and replacing θ by

$\theta_2 = (\varepsilon_{ls} - 2)/3$ for $\text{Ln}J_2 = 0$; it corresponds to $\text{Ln}K_v$ equal to the energy barrier divided by $k_B\theta_2$ written as a function of ε_{ls} . A linear variation of $(\alpha_{2ls})^3$ with $(1 + \varepsilon_{ls})^3 \times \text{Ln}(K_v)$ is then obtained. The relation (1) for a homogeneous liquid combined with (8) leads to $(\alpha_{2ls})^3$ proportional to $\text{Ln}K_v$ as shown in (11) while the relation (2) for a heterogeneous liquid leads to an effective value $(\alpha_{2ls})^3_{\text{eff}}$ proportional to $\text{Ln}(K_{v.v.t})$ instead of $\text{Ln}K_v$ [1]:

$$\alpha_{2sl}^3 = 4(1 + \varepsilon_{ls})^3 \frac{3N_A k_B}{27} \frac{\text{Ln}(K_v)}{16\pi \Delta S_m} \quad (11)$$

The undercooling ratios θ_1 observed on 38 liquid elements [1,2] are much smaller than θ_2 and determined by intrinsic crystals or in few cases by impurity clusters suspended in melts because the energy barrier is reduced by the previous solidification of these surviving crystals. The effective dimensionless surface energy $(\alpha_{1ls})_{\text{eff}}$ is obeying to (12) corresponding to $\text{Ln}(K_{v.v.t}) = 71.9 \pm 1.5$, $v.t = 10^{-8 \pm 1} \text{ m}^3 \cdot \text{s}^{-1}$ and $\text{Ln}K_v = 90$ [6].

$$(\alpha_{1ls})^3_{\text{eff}} \times \Delta S_m = 35.9 \cdot \theta_1^2 (1 + \theta_1) \quad (12)$$

The parameter ε_{ls} is unknown; a new equation is necessary to determine it; equation (13) defines the relation between the critical energy barrier ΔG_2^* for the crystal growth in a homogeneous melt, the observed critical energy barrier ΔG_1^* and the free energy change saving ΔG_{nm} associated to the presence of crystallized nuclei; ΔG_{nm} is given by (5) when R_{2ls} is replaced by the radius R_{nm} of surviving crystals:

$$\Delta G_2^* - \Delta G_1^* = \Delta G_{nm} \quad (13)$$

The critical radius $R_{2ls}(\theta)$ is unchanged in presence or absence of intrinsic nuclei. The crystal growth is occurring at $\theta = \theta_1$ when the crystal radius R_{nm} is equal to $R_{2ls}(\theta_1)$ and ΔG_{nm} is minimum. Then, the derivatives $(d\text{Ln}J_1^*/d\theta)_{\theta=\theta_1}$ and $(d\text{Ln}J_2^*/d\theta)_{\theta=\theta_1}$ are equal because $d\Delta G_{nm}^*/d\theta)_{\theta=\theta_1} = 0$ as written in (14); $(d\text{Ln}J_1^*/d\theta)_{\theta=\theta_1}$ is calculated assuming that $(\alpha_{1ls})^3_{\text{eff}}$ is not temperature dependent because this quantity has been determined under this condition [1]. An effective value $(\alpha_{2ls})_{\text{eff}}$ corresponding to $\text{Ln}(K_{v.v.t}) = 71.9$ is deduced as a function of $(\alpha_{1ls})^3_{\text{eff}}$:

$$\left[\frac{16\pi \Delta S_m (\alpha_{1ls}^3)_{\text{eff}} (3\theta_1 + 2)}{3N_A k_B (1 + \theta_1)^2 \theta_1^3} \right]_1 = \left[\frac{16\pi \Delta S_m (\alpha_{2ls}^3)_{\text{eff}} (3\theta_1 + 2 - \varepsilon_{ls})}{3N_A k_B (1 + \theta_1)^2 (\theta_1 - \varepsilon_{ls})^3} \left(1 - \frac{1 + \theta_1}{1 + \varepsilon_{ls}} \frac{d\varepsilon_{ls}}{d\theta} \right) \right]_2 \quad (14)$$

The dimensionless electrostatic energy ε_{ls} and the new dimensionless surface energy α_{2ls} have been calculated as a function of θ and all homogeneous liquid elements are obeying to the following laws (15) and (16):

$$\alpha_{2ls} \Delta S_m^{1/3} = 1.88 * (1 + \varepsilon_{ls}) \quad (15)$$

$$\varepsilon_{ls} = 0.217 * (1 - 2.5\theta^2) \quad (16)$$

These laws are respected inside the error bar on $\text{Ln}K_v$. Each element has its own value of $\text{Ln}K_v$, α_{2ls} and ε_{ls} ; a variation of K_v by a factor 100 would change $\text{Ln}K_v$ by only by 5%; the dimensionless surface energy α_{2ls} is nearly the same for all elements and weakly increasing with temperature as expected by Turnbull [3]. These similar values for all elements are showing that the surviving intrinsic crystals are spherical because any other shape would induce a dimensionless surface energy variation. The critical energy barrier for crystal growth in a homogeneous melt divided by $k_B T$ is the same for all elements and is diverging for $\theta = -0.196$ or $T_{m2} = 1.196 T_m$. This upper limit for

the existence of unmelted intrinsic crystals is obtained by solving the equation $\varepsilon_{ls}=\theta = 0.217(1-2.5\theta^2)$.

4- The radius of surviving spherical crystals

The presence of surviving crystals in undercooled melts is reducing the free energy change associated to a crystal formation as shown by relation (13) and is precipitating solidification. The radius R_{nm} of such nuclei is obtained by using (13) which is easily transformed in (17):

$$\frac{\alpha_{2ls}^3}{(\theta_1 - \varepsilon_{ls})^2} - \frac{(\alpha_{1ls}^3)_{eff}}{\theta_1^2} = \frac{R_{nm}^3}{4} (\theta_1 - \varepsilon_{ls}) \left(\frac{N_A}{V_m}\right)_{liq} + \frac{3}{4} R_{nm}^2 \alpha_{2ls} \left(\frac{N_A}{V_m}\right)_{liq} \left(\frac{N_A}{V_m}\right)_{sol}^{1/3} \quad (17)$$

The effective energy barrier $\Delta G_1^*(\theta)$ observed for $\theta=\theta_1$ is known [1] and $\Delta G_2^*(\theta)$ is calculated with (8, 15, 16) for $\text{Ln}K_v = 90$ and $\text{Ln}(K_v.v.t) = 71.9$. The quantity ΔG_{nm} is the free energy saving associated with the previous solidification of surviving crystals; it is obtained by replacing R by R_{nm} in (5); $(N_A/V_m)_{sol}$ and $(N_A/V_m)_{liq}$ are the atom numbers per volume unit of solid and liquid at $T=T_m$; two positive solutions are found for R_{nm} ; the smallest one is chosen because R_{nm} is inducing crystal growth at $\theta=\theta_1$ for $\text{Ln}(K_v.v.t) = 71.9$ and has to be smaller than the critical radius $R_{2ls}^*(\theta=\theta_1)$. The ratio $R_{nm}/R_{2sl}^*(\theta=0)$ is about 0.3 for many elements and less than 0.16 only for Ga=0.064, Bi= 0.1, Hg= 0.12, Sn= 0.13, Te= 0.16 because these 5 elements with a low melting temperature have been submitted to larger overheating ratios than the 33 others. The radius R_{nm} and R_{2ls} are represented versus the undercooling ratio $\theta<0$ for copper, aluminum and titanium in figures 1, 2 and 3; θ and R_{nm} are dependent of the overheating temperature of the melt.

The surviving crystal radius cannot increase with the overheating ratio $\theta_s=(T-T_m)/T_m$ in spite of (6) because a droplet can homogeneously grow inside them and reduce their size [13]. Homogeneous nucleation kinetics of a melt in superheated crystals above their melting temperature T_m has been analyzed in order to find the occurrence of a massive homogeneous nucleation temperature of melting in superheated crystals. The critical radius $R_{2ls}(\theta)$ is increasing with $\theta_s>0$ as shown by (6) and diverging for $\theta_s= 0.196$. A mechanism of melting has to take place in order to limit the crystal radius to R_{nm} which could grow up to the droplet volume v without liquid nucleation. The following calculation is made for $\text{Ln}(K_v.v.t) = 71.9$ and also for smaller values taking the activation energy Q for atomic diffusion in surviving crystals into account. It is assumed that the crystals are only melted by homogeneous nucleation of a liquid droplet. To form a liquid spherical nucleus inside a perfect crystalline lattice, the Gibbs free energy change would be:

$$G_l - G_s = \frac{4\pi}{3} R^3 (-\Delta G_v - \varepsilon_v + \Delta E) + 4\pi R^2 \sigma_{2sl} \quad (18)$$

(14): ΔE is the change in the strain energy density per volume unit resulting from the volume change upon melting. It can also be written $\Delta E=f \Delta H_m/V_m$ as a fraction f of the fusion heat per volume unit. The fraction f is small as compared to ΔE is the change in the strain energy density per volume unit resulting from the volume change upon melting. It is written $\Delta E=f \Delta H_m/V_m$ as a fraction f of the fusion heat per volume unit. The fraction f is small compared to ε_{ls} and difficult to evaluate at high temperature; an upper limit of f could be 0.018 for Cu, 0.03 for Ti and Al [14]. The surface energy σ_{2sl} and the electrostatic energy ε_v being proportional to $\text{Ln}K_v$ are modified when $\text{Ln}K_v$ is changed by the diffusion activation energy. The critical energy barrier $\Delta G^*(T)/k_B T$ for a spontaneous liquid growth inside particles is:

$$\frac{\Delta G_{sl}^*(T)}{k_B T} = \frac{16\pi(1.88)^3(1+\varepsilon_{sl})^3}{3N_A k_B (-\theta - \varepsilon_{sl} + f)^2(1+\theta)} \quad (19)$$

A particle cannot have a radius larger than the critical radius R_{2sl} for liquid growth without being rapidly melted.

The surviving particle radius $R_{nm}(\theta)$ are calculated as a function of the overheating ratio θ_s by using (18) and (19) in the following relation $\Delta G_{sl}^*(T)/k_B T - (G_l - G_s)/k_B T = \ln(K_v \cdot v \cdot t) = 71.9$, R being replaced R_{nm} in (18). The $R_{nm}(\theta)$ curves in Figures 1, 2 and 3 have been calculated for $\theta > 0$ with $\ln K_v = 72$ and $\ln(K_v \cdot v \cdot t) = 54$ for aluminium and titanium and $\ln K_v = 82$ and $\ln(K_v \cdot v \cdot t) = 64$ for copper. The growth critical radius R_{2sl} of liquid droplet of Cu, Al and Ti are also plotted versus θ_s . The particle radius R_{nm} producing a spontaneous solidification for $\theta = \theta_1$ after a quench from θ_s , is represented by a parallel to the θ axis in Figures 2, 3 and 4. The calculated superheating ratios θ_s for Cu, Al and Ti respectively leading to the undercooling ratios $\theta_1 = 0.19, 0.17$ and 0.17 are equal to $0.167, 0.15$ and 0.155 . These values explain why θ_1 is seen as a limit of the undercooling ratio of each element far from $-2/3$ in spite of the application of large overheating ratios θ_s (nevertheless not larger than 0.196).

An overheating interval in which the largest particles have a stable radius up to θ_c can exist as shown in Figures 1 and 2. The radius $R_{nm}(\theta=0)$ can stay unchanged up to θ_c and the processing time can be strongly increased without melting up to θ_c . They melt progressively with time and temperature above θ_c and their radius are following the $R_{nm}(\theta)$ curves calculated for the same value of $v \cdot t$ and their time dependence is very weak. The θ_c existence has been already observed for several compounds [11] and in particular for Dy_3Al_2 ($f=0.01$). This compound is textured after solidification in a magnetic field when θ remains smaller than θ_c . Crystal growth can take place at $T=T_m$ leading to bigger particles free to align in a magnetic field. Solidification starts at smaller temperatures than T_m from surface heterogeneities or from intrinsic nuclei smaller than the radius $R_{nm}(0)$ for crystal growth. For Dy_3Al_2 , after an overheating ratio $\theta < \theta_c$, the solidification in a magnetic field leads to crystal alignment without recalescence. After an overheating above θ_c , an undercooling is observed followed by recalescence accompanying solidification without texturing [11].

Figures 1, 2 and 3: The critical radius R_{2ls} and R_{2sl} of crystal and liquid growths and the radius R_{nm} of surviving crystals are plotted versus $\theta_1 < \theta < 0.196$. The strain energy density is a fraction f of the fusion heat per volume unit. In Figure 1, 2 and 3, the calculations of R_{nm} for $\theta > 0$ with $f = 0.018$, $\text{Ln}K_v = 82$ and $\text{Ln}(K_v.v.t) = 64$ for Cu, $f = 0.03$, $\text{Ln}K_v = 72$ and $\text{Ln}(K_v.v.t) = 54$ for Al, $f = 0.03$, $\text{Ln}K_v = 72$ and $\text{Ln}(K_v.v.t) = 54$ for Ti. The radius R_{nm} for $\theta < 0$ corresponds to $\text{Ln}K_v = 90$ and $\text{Ln}(K_v.v.t) = 71.9$; the surface energy proportional to $\text{Ln}K_v$ has been modified. The surviving crystal size $R_{nm}(\theta=0)$ is stable from $\theta = 0$ to θ_c for Ti and Cu and is slightly decreasing for Al.

5- Conclusion

A new analysis of undercooling experiments related to the crystal nucleation- growth phenomena is proposed in this contribution:

- Tiny crystals are surviving above the melting temperature T_m of 38 elements.
- These crystals act as intrinsic growth nuclei in undercooled liquids and precipitate the solidification because their presence is reducing the critical energy barrier for nucleation in homogeneous liquids.
- A negative contribution $-\varepsilon_v = -\varepsilon_{ls}\Delta H_m/V_m$ to the Gibbs free energy change for a crystal formation is missing in the classical growth nucleation model, $\Delta H_m/V_m$ being the fusion heat per unit volume. This quantity is stabilizing tiny crystals above the melting temperature.
- This missing contribution represents the same fraction ε_{ls} of the fusion heat per unit volume of 38 elements and is varying with the undercooling ratio $\theta = (T - T_m)/T_m$; $\varepsilon_{ls} = 0.217(1 - 2.5\theta^2)$ becomes negligible for $\theta \cong -0.63$. This disappearance is occurring when the free volume becomes negligible in agreement with observations of the free volume disappearance in metallic amorphous alloys for $\theta = -0.66$.
- The dimensionless surface energy α_{2ls} is given by a unique formula for the 38 elements $\alpha_{2ls}\Delta S_m^{1/3} = 1.88(1 + \varepsilon_{ls})$ because the characteristic frequency K_v per volume unit and per second acting as a prefactor in the nucleation rate for a crystal formation is weakly varying with elements.
- The surviving crystals could melt at a second fusion temperature $T_{m2} = (1 + \varepsilon_{ls}) T_m = 1.20 T_m$.
- The transfer of conduction electrons from the solid to the liquid or from the liquid to the solid is inducing an interface electrostatic interaction that is missing in the Gibbs free energy change used in the classical nucleation- growth model for a crystal formation.
- This analysis is confirming that the classical nucleation-growth model, when completed, is very efficient to describe the experimental properties of melts.

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in a magnetic field could be induced by intrinsic nuclei. Some references to their work are given in [11]

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