

THE DETERMINATION OF THE SOLID-LIQUID
INTERFACIAL TENSION IN GERMANIUM

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Germanium is one of the numerous materials which still can not be prepared in a glass state by the existing quenching methods⁽¹⁾. It has been shown⁽²⁾ that Ge has to be cooled at the rate of at least above 10^7 K/s, which is the upper limit for the splat quenching. Thus, in order to prepare Ge in a glass state one needs to improve the cooling rate, which is approximately given by the following general formula for heat conduction:

$$Q = \frac{(T_m - T_a)}{\rho c} \frac{h}{D} \quad (1)$$

where, T_m and T_a are the melting and the ambient temperature respectively, c thermal capacity, h heat transport coefficient, ρ density, and D dimension of the sample in heat flow direction. In quenching methods the lowest dimensions of samples are around $5 \mu\text{m}$ so that the cooling rate limit is about 10^7 K/s.

In this work⁽³⁾ the forced convection as a cooling method has been used. Actually, liquid Ge under the pure argon atmosphere was dispersed in the cloud of small spheres with diameters ranging from $0.01 \mu\text{m}$ to $5 \mu\text{m}$. The heat transport coefficient is⁽⁴⁾:

$$h = \frac{\mathcal{K}}{D} (20 + 0.6 \left(\frac{vD}{\nu'}\right)^{1/2} \left(\frac{c' \rho'}{\mathcal{K}'}\right)^{1/3} \quad (2)$$

where, \mathcal{K}' , ν' , c' and ρ' are constants for an inert gas, v velocity of spheres and \mathcal{K} thermal conductivity of Ge. Such range of diameters allows the use cooling rates between 10^{10} K/s and 10^4 K/s.

The samples were carefully examined by the electron microscope, by looking at their structural properties and by measuring the diameters. It has been found that Ge spheres with diameter of $D \leq 0.3 \mu\text{m}$ were glassy, while those with $D > 0.3 \mu\text{m}$ were partially or entirely crystal-

l line.

Thus, Ge has to be cooled at the rate at least 4×10^8 K/s in order to prevent crystallization entirely. The fact that there is the maximum possible diameter of glassy Ge spheres and that they are cooled by the minimum rate is used for the determination of solid-liquid interfacial tension.

The framework of homogenous nucleation theory and the Turnbull's approach⁽⁵⁾ in examining the formation of crystal nuclei in a liquid has been used. Turnbull's expression for the steady state homogenous nucleation frequency rate, is:

$$I_0 = \frac{NRT_m}{3\pi M^2 \eta(\frac{T}{T_m})} \exp\left(-\frac{16\pi}{3} \frac{\Delta H_m}{RT_m}\right) \propto^3 \frac{1}{\left(\frac{T}{T_m}\right)^3 \left(1 - \frac{T}{T_m}\right)^2} \quad (3)$$

where, N, R, M are Avogadro's number, gas constant and molecular weight respectively, $\eta(\frac{T}{T_m})$ temperature dependent viscosity, ΔH_m molar heat of fusion and α reduced solid-liquid interfacial tension. The α is defined by $\frac{(N\bar{v}^2)^{1/3} \cdot \sigma_{sl}}{\Delta H_m}$ where σ_{sl} is solid-liquid interfacial tension and \bar{v} molar volume of a stable nucleus. Also, the Turnbull's criterion for a glass definition has been adopted; the sample is considered as crystalline if a stable nucleus is formed. This is expressed by the Vreeswijk's formula⁽⁶⁾:

$$V_c \int_{T_m}^{T_g} \frac{I_0 \exp\left(-\frac{3\pi^2 M \eta Q_c}{Rg(T_m - T)T}\right)}{Q_c} dT = 1 \quad (4)$$

which contains the time transient function to describe the fast cooling process, in our case. The T_g is the glass transition temperature. V_c and Q_c are critical volume and cooling rate respectively. In accordance with (1), (2), and (3) and under the assumption that viscosity is known within the whole temperature range, the integral can be solved by means of finding the pairs of values for α and D_c .

The viscosity function was constructed by fitting the Fulcher's relation $\eta = \eta_0 \exp\left(\frac{a}{T - T_0}\right)$: with the experimental data above the melting point⁽⁶⁾, and with the conventional

magnitude of viscosity at T_g - $\eta(T_g) = 10^{15}$ Poise⁽⁵⁾. The measurements gave the critical diameter of $D_c = (0.30 \pm 0.05) \mu\text{m}$. This implies $\alpha = (0.270 \pm 0.005)$ and $\sigma_{cs} = 167 \text{ ergs cm}^{-2}$. The result is 10% lower than the Turnbull one - $\sigma_{cs} = 181 \text{ ergs cm}^{-2}$ ⁽⁷⁾. In order to give qualitative explanation for this disagreement the similarities and differences between the two methods are briefly discussed below. The Turnbull's experiment is done under following conditions: the liquid spheres with diameters around $400 \mu\text{m}$ were supercooled at the rate of approximately 1 K/s ; the beginning of the crystallization was observed by the optical microscope. The α was calculated under almost the same conditions mentioned in this paper.

In the present case the whole nucleation frequency curve has been taken into account; the probability of heterogeneous nucleation events has been lowered by factor of $\sim 10^9$ in dealing with spheres having diameters $\sim 10^3$ times lower.

The result was tested by using other existing experimental data: the unsuccessful attempt to prepare glassy Ge by the splat cooling method resulted with the lower limit for the cooling rate of at least about 10^7 K/s . The upper limit was established by the lowest possible diameter of Ge spheres of 10^8 \AA . Due to forced convection method of cooling the corresponding rate is 10^{12} K/s .

Using these limits α can be delimited between 0.25 and 0.29. Therefore the resulting α of 0.27, together with the corresponding cooling rate of $4 \times 10^8 \text{ K/s}$ is fairly reasonable.

References

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