CHAPTER 6

DETERMINATION OF CONFIGURATIONAL ENTROPY AND STABILITY LIMIT OF A BULK METALLIC GLASS FROM THERMAL EXPANSION MEASUREMENTS
6.1 Introduction

Our understanding of the glass state is still far from complete inspite of the fact that glass making was discovered long ago [1]. A very large number of materials can now be produced in the glassy or amorphous state and the techniques of making them are equally varied e.g., rapid quenching of melt [2-4], vapour deposition on cold substrate [5], electro-deposition [6], electron beam irradiation [7,8], solid state amorphisation by hydrogen dissolution or thermal interdiffusion of two elemental polycrystalline metals [9,10], high energy mechanical ball milling [11-15], etc. Glasses differ structurally from the crystalline solids in the absence of long range lattice order as shown by X-ray diffraction [16]. Other new and technologically important physical properties of glassy materials make them very useful for applications [17].

The conventional root to making a glassy solid by undercooling of melt has been more widely used for a long time and better understood as compared to the other recent methods of solid state amorphisation. Ordinarily a liquid will solidify by the process of nucleation and growth of crystals into a crystalline solid if cooled below the melting temperature and left for sufficient time. The nucleation rate increases with increase in undercooling temperature. However if the liquid is cooled rapidly it can continue to remain in the undercooled state and a configurational freezing of the atomic arrangement of the liquid state takes place at a temperature $T_g$ (which is termed as the Glass transition temperature), because there is not enough time for atomic rearrangements to lead to a crystalline atomic configuration [1,16]. The glass transition temperature however depends a little in the cooling rate but is nevertheless taken to be a well defined transition temperature [1].
Fig. 6.1 shows a schematic illustration of the change in thermodynamic variables such as volume (V), entropy (S) or enthalpy (H) across a liquid Co crystal or supercooled liquid to glass transformation [16]. The glass transition is accompanied by a change in slope of these thermodynamic variables and differential quantities such as thermal expansion coefficient (\(a\)) and specific heat (C) therefore show a discontinuity at \(T_g\) suggesting a second order like behaviour. Without going into less definitive and contentious issues such as whether the glass transition is a truly second order transition because of the kinetic dependence of \(T_g\), or whether the glass state is truly equilibrium thermodynamic state, the glass and the supercooled liquid states are treated on the same footing and a quantitative understanding of the thermodynamic quantities such as free energy and entropy difference between supercooled liquid and crystalline states has been made [16]. However very little is said about the thermodynamic functions of the actual glass state itself which is fundamentally different from the supercooled liquid phase at least in one aspect viz - the translational degrees of freedom which exist in the liquid phase get frozen in the glass phase.

### 6.1.1 Bulk Metallic Glass

Metallic alloys require very high quenching rates, of the order of \(10^6 K/sec\) or so, to form glasses. These metallic glasses are very important technologically, as they show high fracture strength, excellent soft magnetic behaviour and good corrosion resistance [18]. But the high quenching rate of the melt for the glass formation, has restricted the physical dimensions of these glasses to thin ribbons. During past several years a lot of effort has gone into finding systems from which glasses can be made in bulk form with ease. Recently it has been possible to obtain metallic
Fig. 6.1: A schematic illustration of the change in volume across a liquid to crystal and supercooled liquid to glass state. A change in slope is seen at the glass transition temperature between the liquid and the glass state and a jump at $T_M$ between the liquid and the crystal.
glasses in some alloy systems such as Zr - Ni - Cu - Al [19], La - Al - Ni [20], Mg - Cn - Y [21] and Zr - Ni - Tl - Cu [22] at low cooling rates. These glasses therefore can be fabricated in bulk dimensions and can also be processed for technological applications as the temperature interval $\Delta T_x$ between the glass transition temperature ($T_g$) and the crystallization temperature ($T_x$) is quite large in these materials. To understand the glass forming ability and their phase stability against crystallization it is essential to have estimates of various thermodynamic parameters. In this work a simple method is used to estimate the configurational entropy of glass by calculating its total entropy from thermodynamic considerations and subtracting from it the vibrational and electronic entropies obtained from thermal expansion measurements. Gibb's free energy difference between the glassy and the crystalline states has been calculated, which gives a measure of the thermal stability of the glass state. Here, a bulk metallic glass of composition $Zr_{63}Ni_{10}Cu_{5}Al_{12.5}$ is used which has a high AT, value (= 112 K) to calculate the vibrational, electronic and configurational entropies in the glassy as well as crystalline states.

6.2 Sample preparation

The samples were prepared by arc melting requisite quantities of Hafnium free Zr (99.5% purity) and high purity Cu, Ni and Al in an Edmund Bühler D-7400 arc melting furnace under a Ti gettered argon atmosphere. There was negligible weight loss after melting. The alloy ingot was cut into small pieces and transferred to a Vycor glass tube of 7 mm inner diameter constricted to 4 mm diameter at one end. After induction melting the melt was injected into copper moulds by application of slight gas pressure from the other end of the Vycor tube. Rectangular blocks of
dimensions 22.5 x 5 x 3 mm\(^3\) were cast by this procedure. The surface of the moulded sample was polished to remove the crystallized phase which formed in contact with the copper mould. The bulk sample obtained was amorphous as confirmed by the X-ray diffraction pattern recorded with Inel position sensitive detector using Co K\(_\alpha\) radiation (\(\lambda = 0.1790\) nm) (see Fig.G.2).

**Fig.6.3** shows the Differential Scanning Calorimetry (DSC) measurements on the sample. The DSC measurement has been done with a heating rate of 10 C per minute. The glass transition temperature \(T_g\) came out to be 624 K (see the inset (a) of Fig.6.3) which compares well with the value of \(T_c = 623\) K for the sample of same composition given in literature [19]. The crystallization temperature came out to be \(T_X = 736\) K (inset (b) of Fig.6.3).

### 6.3 Thermal Expansion Measurements

A sample of cuboid shape and dimensions 3 x 2.5 x 1.2 mm\(^3\) was cut from the main block for thermal expansion measurements. The sample was cut carefully to have parallel faces. The faces were polished to have a smooth surface. The thermal expansion measurements were carried out using the three terminal capacitance dilatometer as described in Chapter 2. The sample temperature was scanned at the rate of 2 mK/sec and the capacitance values were recorded at intervals of 4 sec. An average of fifty readings was taken to get the observations at 0.4 K intervals. The glass sample was then crystallized by heat treating it at 873 K for a period of 24 hrs and thermal expansion measurements were carried out on the crystallized sample.

**Fig.6.4** shows the fractional length change \(\Delta L(T) / L(T_0)\) data as a function of
Fig. 6.2: The X-ray diffraction patterns of $Zr_{65}Ni_{10}Cu_{17.5}Al_{7.5}$ bulk metallic glass (G) and of its crystalline state (X) recorded with Inel position sensitive detector using Co $K_\alpha$ radiation.
Fig. 6.3: Differential Scanning Calorimetry measurements with a heating rate of 10 degree Celsius per minute on Zr_{65}Ni_{10}Cu_{17.5}Al_{7.5} bulk metallic glass. Insets (a) and (b) show the values of $T_g$ and $T_X$ respectively.
temperature in both glassy and crystalline phases. In the figure every fifth data point is plotted for better clarity. Fig. 6.5 shows the variation of thermal expansion co-efficient \( \alpha(T) = \frac{\Delta L}{\Delta T} \) as a function of temperature as obtained directly from the measured fractional length change data by numerical three point differentiation. As expected the thermal expansion of glass shows less change with temperature than that of the crystal.

6.4 Data Analysis

The fractional length change data is analyzed using the anharmonic model described in Chapter 3. The \( \Delta L(T)/L(T_0) \) data is fitted to the expression

\[
\frac{\Delta L(T)}{L(T_0)} = \frac{\langle x \rangle_T - \langle x \rangle_{T_0}}{a(T_0)}
\]

where \( \langle x \rangle_T \) is the average lattice displacement at temperature \( T \) which is given by the expressions (3.4), (3.14) and (3.24) and reproduced here for continuity,

\[
\langle x \rangle_T = a(T_0) \frac{\gamma_{el}}{2} T^2 + \frac{3g}{4c^2} \left\{ \varepsilon - \left( \frac{15g^2}{16c^2} - \frac{8f}{c^2} \right) \varepsilon^2 - \frac{35}{16} \left( \frac{15g^2f}{4c^5} + \frac{3f^3}{c^4} \right) \varepsilon^3 \right\} \tag{6.2}
\]

\[
\varepsilon = \left\{ \left( \frac{3}{p} \right) \frac{k_B T}{(T/\Theta_D)^3} \right\} + \int \frac{e^z}{e^z - 1} + \left( \frac{p - 3}{p} \right) \frac{k_B \Theta_E}{e^{\Theta_E/T} - 1}
\]

\( \gamma_{el} \) gives a measure of the electronic contribution to the lattice displacement. \( \Theta_D \) and \( \Theta_E \) are respectively the Debye and Einstein temperatures and \( p \) is the average number of phonon branches actually excited over the entire range of temperature.

The fitting of the experimental data was done using \( \gamma_{el}, g' = g/c^2 \lambda, g'' = g^2/c^3 \) and \( f = f/c^2 \Theta_D, p \) and \( \Theta_E \) as parameters. The solid lines in figs. 6.4 and 6.5 show
Fig. 6.4: Fractional length change data as a function of temperature for the crystalline and the glassy Zr$_{65}$Ni$_{10}$Cu$_{17.5}$Al$_{7.5}$alloy. The solid line represents the fits to the data using eqns. (6.1) and (6.2).
Fig.6.5 : Measured thermal expansion coefficient (α) data as a function of temperature for the crystalline and the glassy Zr$_{65}$Ni$_{10}$Cu$_{17.5}$Al$_{5}$ alloy. The solid line shows the analytic derivative of eqn.(6.1).
the fits. The fits in both the glass and crystalline phases are excellent with a r.m.s. deviation is of about 0.2%. Table-6.1 shows the values of the fitted parameters.

The anharmonicity parameters \( g'' \) and \( \gamma' \) have increased by quite large amount in the glass phase as compared to the crystal phase. The large increase in the quartic anharmonicity parameter \( \gamma' \) shows softening of lattice in the glass and suggests that the lattice potential becomes more shallow as compared to the crystal phase. The glass phase does not show any optic mode whereas the crystal phase gives an average of 7.5 optic modes with an Einstein temperature of 494.7 K which is lower than the Debye temperature 582.0 K. The value of electronic parameter \( \gamma \) in the crystal phase is twice that of the glass phase.

A check on the consistency of the parameters obtained for the fits to thermal expansion data can be made by calculating the total specific heat (vibrational+electronic) and comparing with experimental results on specific heats of the system. This consistency is shown in the next section.

6.5 Calculation of Specific Heat

As described in the chapter 3, the vibrational specific heat \( C_{ph} \) is calculated using the relation [23] (see also eqn.(3.18))

\[
C_{ph} = 3N \varepsilon' - 6N \left( \frac{15 g''^2}{8 e^3} - \frac{3 f'}{4 e^2} \right) \varepsilon \times \varepsilon'
\]

where,

\[
\varepsilon' = \left\{ \frac{3}{p} \right\} 3k_B \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_E} \frac{e^{\frac{\Theta_E}{T}} \varepsilon^4 e^z}{(e^z - 1)^2} dz + \left( \frac{p - 3}{p} \right) k_B \left( \frac{\Theta_E}{T} \right)^2 \frac{e^{\frac{\Theta_E}{T}}}{(e^{\frac{\Theta_E}{T}} - 1)^2} \right\}
\]
### Table-6.1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Glass</th>
<th>Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Theta_D (K)$</td>
<td>562.3+08</td>
<td>582.6+07</td>
</tr>
<tr>
<td>$g' (eV)$</td>
<td>0239+0 008</td>
<td>0 251±0.007</td>
</tr>
<tr>
<td>$g'' (eV^{-1})$</td>
<td>(165.531±0.8)×10^{-3}</td>
<td>(2.972±0.06)×10^{-3}</td>
</tr>
<tr>
<td>$f (eV^{-1})$</td>
<td>(207.833±0.8)×10^{-4}</td>
<td>(3.488±0.06)×10^{-4}</td>
</tr>
<tr>
<td>$\gamma_{el} (K^{-2})$</td>
<td>(4.686±0.06)×10^{-9}</td>
<td>(8.987±0.07)×10^{-9}</td>
</tr>
<tr>
<td>$p$</td>
<td>3.</td>
<td>10.5±0.03</td>
</tr>
<tr>
<td>$\Theta_1 (K)$</td>
<td>-</td>
<td>494.7±0.3</td>
</tr>
</tbody>
</table>

The characteristic Debye and Einstein temperatures and the anharmonicity parameters obtained from the fit of the fractional length change data in both the glassy and crystalline states.
and \( N \) is the Avogadro number. Fig. 6.6 shows \( C_{\text{pi}} \) for both the glass and the crystal phases, calculated using the fitted parameters \( p, \Theta_D, \Theta_E, g'' \) and \( \lambda' \). As expected \( C_{\text{ph}} \) for the glassy phase is more than the crystalline phase.

The electronic specific heat is calculated using the relation [24],

\[
C_{el} = \frac{3B_f V \gamma_{el} T}{\Gamma_{el}^f}
\]  

(6.5)

Where \( B_f \) is the isothermal bulk modulus, \( V \) is the molar volume, and \( \Gamma_{el}^f \) is the electronic Grüneneisen parameter. The experimental values of the Young's modulus of \( Zr_{65}Ni_{10}Cu_{12.5}Al_5 \) alloy in the glassy and the crystalline phases are measured to be 72 GPa and 117 GPa [25] respectively. By taking a weighted average of the Poisson's ratio for this material, which come out to be 0.36, the bulk modulii are calculated. The bulk modulii \( B_f \) are estimated to be 85.7 GPa and 139.3 GPa in glassy and crystalline phases respectively. The molar volume of the above alloy in the glassy phase is measured to be 11.79 cc whereas it is 12.07 cc for the crystalline phase. Using the above mentioned experimental values of \( B_f \) and \( V \) and taking the electronic Grüneneisen parameter as 2/3 which is the free electron value, the \( C_{el} \) is calculated for both the states. The total specific heat \( (C_{el} + C_{\text{ph}}) \) calculated using the parameters obtained from our thermal expansion data compares very well (within 6%) with the experimental specific heat as reported by Zhang et. al. [19] in the temperature range 400 K to 620 K (see Fig. 6.7). This gives confidence in our method of calculating the vibrational and electronic entropies. Next we find the total entropy difference between glass and crystalline states from thermodynamic consideration and subtract from it the vibrational and electronic entropy to get the configurational entropy.
Fig. 6.6: Vibrational contribution to specific heat calculated using the fitted parameter values for the crystalline and the glassy Zr$_{65}$Ni$_{10}$Cu$_{17.5}$Al$_{7.5}$ alloy.
Fig. 6.7: Total specific heat \( C = C_{el} + C_{ph} \) of the glass calculated using the parameters obtained from our thermal expansion data fitting compared with the specific heat data of Zhang et.al. taken from ref. 19.
6.6 Estimation of Thermodynamic Parameters

6.6.1 Supercooled Liquid State

From Fig. 6.8 the entropy difference between the supercooled liquid and the crystal at a temperature $T < T_M$ is given by

$$\Delta S^{LX}(T) = \Delta S_M + \int_{T_M}^{T} \frac{\Delta C_{p}^{LX}}{T} \, dT$$  \hspace{1cm} (6.6)

Where $\Delta S^{LX}(T)$ is the entropy difference between the supercooled liquid and the crystal at any temperature $T$, $\Delta S_M$ is the entropy of fusion at the melting temperature $T_M$ and $\Delta C_{p}^{LX}$ is the specific heat difference between the supercooled liquid and the crystal.

The enthalpy difference between the supercooled liquid and the crystal ($\Delta H^{LX}$) can be calculated as follows.

$$\Delta H^{LX} = \int_{T_X}^{T_L} dQ = \int_{T_X}^{T_M} C_{p}^{X} \, dT + \int_{T_M}^{T} dQ + \int_{T_M}^{T} C_{p}^{L} \, dT$$

$$= - \int_{T_M}^{T} C_{p}^{X} dT + T_M \Delta S_M + \int_{T_M}^{T} C_{p}^{L} dT$$

$$= T_M \Delta S_M + \int_{T_M}^{T} \Delta C_{p}^{LX} \, dT$$  \hspace{1cm} (6.7)

The Gibbs free energy difference, $\Delta G^{LX}$ being the driving force for crystallization, which measures the ability for glass formation is calculated as,

$$\Delta G^{LX}(T) = T_M \Delta S_M + \int_{T_M}^{T} \Delta C_{p}^{LX} \, dT - T \Delta S_M - T \int_{T_M}^{T} \frac{\Delta C_{p}^{LX}}{T} dT$$  \hspace{1cm} (6.6)

The entropy of fusion $\Delta S_M$ can be calculated as $[26]$. 

Fig. 6.8: A schematic illustration for the calculation of the entropy difference $\Delta S_{lx}$ between the supercooled liquid and crystal states. Arrow heads indicating the path to be followed.
Now if one assumes $\Delta C_p^{LX}$ is constant up to a temperature which is not much below $T_M$ then, eqn. (6.10) can be written as.

$$\int_0^{T_M} C_p^L dT - \int_0^{T_M} C_p^X dT = T_M \Delta S_M$$  \hspace{1cm} (6.9)$$

or,

$$\int_0^{T_M} \Delta C_p^{LX} dT = T_M \Delta S_M$$  \hspace{1cm} (6.10)$$

By substituting the value for $\Delta C_p^{LX}$ in the expressions for $\Delta S^{LX}(T)$, $\Delta H^{LX}(T)$ and $\Delta G^{LX}(T)$ the eqns. (6.6), (6.7) and (6.8) can be approximated as,

$$\Delta S^{LX}(T) = \Delta S_M - \Delta S_M \ln \left( \frac{T_M}{T} \right)$$  \hspace{1cm} (6.13)$$

$$\Delta H^{LX}(T) = T \Delta S_M$$  \hspace{1cm} (6.14)$$

$$\Delta G^{LX}(T) = T \Delta S_M \ln \left( \frac{T_M}{T} \right)$$  \hspace{1cm} (6.15)$$

### 6.6.2 Glass State

To reach the glass state one goes to temperature $T < T_g$ as shown in Fig. 6.9 The entropy difference between glass and crystal, $\Delta S^{GX}(T)$ at a temperature $T < T_g$
Fig. 6.9: A schematic illustration of entropy in the supercooled liquid, glass and the crystal states of the same material. The arrow heads indicate the path to be followed for the calculation of $\Delta S^{\text{GX}}(T)$. 
can be calculated as,

$$\Delta S^{Gx}(T) = \int_{T_g}^{T} dS = \int_{T_g}^{T} \frac{T_g}{T} dT + \int_{T_g}^{T} \frac{T_g}{T} dT + \int_{T_g}^{T_g} \frac{T_g}{T} dT + \int_{T_g}^{T_g} \frac{T_g}{T} dT$$

$$= \int_{T_g}^{T} \frac{C_P^X}{T} dT + \int_{T_g}^{T} \frac{C_P^X}{T} dT + \Delta S_M + \int_{T_g}^{T} \frac{C_P}{T} dT + \int_{T_g}^{T} \frac{C_P}{T} dT$$

$$= \Delta S_M + \left( \int_{T_g}^{T} \frac{C_P}{T} dT - \int_{T_g}^{T} \frac{C_P}{T} dT \right) + \left( \int_{T_g}^{T} \frac{C_P}{T} dT - \int_{T_g}^{T} \frac{C_P}{T} dT \right)$$

$$\Delta S^{Gx}(T) = \Delta S_M + \int_{T_g}^{T} \frac{C_P^X - C_P^X}{T} dT + \int_{T_g}^{T} \frac{\Delta C_P^{LG}}{T} dT \quad (6.16)$$

If we take a temperature near $T_g$, when $C_p$ can be approximated as $C_p = C_p - \Delta C_P^{LG}$, where $\Delta C_P^{LG}$ is the specific heat jump at $T_g$ when the supercooled liquid freezes into a glass. Then by rewriting the equation (6.16) as,

$$\Delta S^{Gx}(T) = \Delta S_M + \int_{T_g}^{T} \frac{\Delta C_P^{LG}}{T} dT + \int_{T_g}^{T} \frac{C_P^I - \Delta C_P^{LG} - C_P^X}{T} dT$$

$$\Delta S^{Gx}(T) = \Delta S_M + \int_{T_g}^{T} \frac{\Delta C_P^{LG}}{T} dT + \int_{T_g}^{T} \frac{\Delta C_P^{LG}}{T} dT - \int_{T_g}^{T} \frac{\Delta C_P^{LG}}{T} dT \quad (6.17)$$

Now substituting for $\Delta C_P^{LG} = \Delta S_M$ and taking $\Delta C_P^{LG}$ as the jump at $T_g$ and assuming that $T$ is not much below $T_g$,

$$\Delta S^{Gx}(T) = \Delta S_M - \Delta C_P^{LG} \ln \left( \frac{T_M}{T} \right) + \Delta C_P^{LG} \ln \left( \frac{T_g}{T} \right) \quad (6.18)$$

Similarly the enthalpy difference between the glass and the crystal can be written as,

$$\Delta H^{Gx}(T) = T_M \Delta S_M - \Delta C_P^{LG} (T_M - T) + \Delta C_P^{LG} (T_g - T)$$
So the Gibb's free energy difference \( (\Delta G^G) \) between the glass and the crystal which shows the stability of the glass can be estimated as,

\[
\Delta G^G(T) = \Delta H^G(T) - T \Delta S^G(T)
\]

6.7 Estimation of Configurational Entropy of the Glass

The vibrational and the electronic entropies \( (S_{ph} \text{ and } S_{el}) \) of the glassy and the crystalline forms of the sample are calculated using the relation,

\[
S_{ph} = \int_0^T \frac{C_{ph,el}}{T} dT
\]

Assuming the crystal does not have any configurational entropy, the total entropy of the crystalline sample can be given by,

\[
S^X = S_{ph}^X + S_{el}^X
\]

The total entropy of the glassy alloy can be written as,

\[
S^G = S_{ph}^G + S_{el}^G + S_{conf,g}^G = S^X + \Delta S^G
\]

Where \( S_{conf,g}^G \) is the configurational entropy of the glass and the expression for \( \Delta S^G \) is given by equation (6.18).

For the present \( Zr - Ni - Cu - Al \) sample the total crystalline entropy is calculated using the eqn.(6.22). Then for estimating total entropy of glass \( S^G \), eqn.(6.23)
is used by taking the value of $\Delta S^{G,X}$ which is estimated using eqn.(6.18). Similarly the total entropy for the supercooled liquid state is estimated by adding $\Delta S^{L,X}$ (calculated using eqn.(6.13)) to $S^X$. Fig.6.10 shows the temperature dependance of $S^G$, $S^L$ and $S^X$. As expected the supercooled liquid freezes into glass at $T_g(=624 \text{ K})$ where the entropy curve shows a slope change indicating a second-order phase transition-like behaviour. The Kauzman temperature [27] $T_{t,LX}^i$ calculated from the insentropic condition $\Delta S^{L,X} = 0$ is found to be $T_M/c$, where $c$ is the base of the Naperian logarithm.

The vibrational entropy ($S_{ph}^G$) and the electronic entropy ($S_{el}^G$) are calculated from $C_{ph}^G$ and $C_{el}^G$ respectively. The vibrational and electronic specific heat is calculated from the fitted parameters obtained from the fit of the thermal expansion data of the bulk metallic glass. The configurational entropy ($S_{config}^G$) of the glass then is estimated by subtracting ($S_{ph}^G + S_{el}^G$) from $S^G$. The temperature dependance of $S_{config}^G$ together with $S_{ph}^G$ and $S_{el}^G$ is given in the inset of fig.6.10. The magnitude of the configurational entropy of the bulk metallic glass in a small temperature range below $T_G$ comes out to be 17 J/mol K. The configurational entropy of an ideal solid solution with n-components can be calculated as [28],

$$S_{config} = -R \sum_{i=1}^{n} X_i \ln X_i$$  \hspace{1cm} (6.24)

where $X_i$ is the concentration of the $i^{th}$ component. The configurational entropy of the ideal solid solution of the composition $Zr_{65}Ni_{10}C_{8}Al_{15}$ is calculated as 8.45 J/mol K which is half of the estimated configurational entropy of the glass.

Another interesting result which comes out from this analysis is that one can define a new instability temperature $T_{t,GX}^i$ from the isentropic condition, $\Delta S^{G,X} = 0$ which gives the limiting temperature upto which a glass could be superheated.
Fig. 6.10: Total entropy of the crystalline, glassy and the supercooled liquid phases of the bulk metallic glass $Zr_{65}Ni_{10}Cu_{17.5}Al_{7.5}$ as a function of temperature. The curve for the glass phase between $T_g$ and $T_i^{CX}$ represents the superheated region. The electronic, vibrational and configurational entropy contributions of the glass are shown in the inset.
without being allowed to go into the liquid phase. For the bulk metallic glass used in this work, \( T_f^{g2} \) is found out to be \( 730 \, \text{K} \) (see Fig.6.10). A similar isentropic instability temperature for a superheated crystal was defined by Fecht and Johnson [29].

The enthalpy differences \( \Delta H^{LX} \) and \( \Delta H^{GX} \) are obtained using the eqns.(6.14) and (6.19). The Gibb's fee energy differences \( \Delta G^{LX} \) and \( \Delta G^{GX} \) are calculated using eqns(6.15) and (6.20) as a function of temperature and are plotted in Fig.6.11. One see's that \( \Delta G^{LX} \) and \( \Delta G^{GX} \) touch each other at \( T_g \). At a undercooling of 100 K below \( T_M, \Delta G^{LX} = 377.9 \, \text{J/mol} \) which gives a very small driving force for crystallization indicating a good glass forming ability of these glasses. Similarly the excess Gibb's free energy \( \Delta G^{GX} \) of the superheated glass relative to the corresponding crystalline form at a temperature 100 K above \( T_g \) is found to be \( 1.24 \, \text{KJ/mol} \) which gives a measure of the stability of the glassy phase.

6.8 Conclusion

The thermal expansion co-efficient around room temperature is found out to be less in the case of the bulk metallic glass \( \text{Zr}_{65}\text{Ni}_{15}\text{Cu}_{15}\text{Al}_{7.5} \) than that in the corresponding crystalline phase. From the fit to our model the Debye temperatures are found out to be \( 562.3 \, \text{K} \) and \( 582.6 \, \text{K} \) for the glassy and crystalline states respectively. The glassy phase does not show any optic mode whereas the crystalline phase gives an Einstein temperature \( \Theta_E = 494.7 \, \text{K} \) with 10.5 as the average number of total excited modes (acoustic and optic). The total entropies \( S^X, S^L \) and \( S^G \) are calculated. The configurational entropy of the glass is found out to be \( 17 \, \text{J/mol K} \) just below \( T_g \). A new isentropic temperature \( T_f^{g2} = 730 \, \text{K} \) is predicted upto which
Fig. 6.11: Gibb’s free energy differences $\Delta G^{LX}$ and $\Delta G^{GX}$ as a function of temperature calculated using eqns. (6.15) and (6.20) respectively.
this glass can be superheated. The Gibb's free energy difference between the glass and the crystal is estimated which gives a measure of the stability of the glassy state. The driving force $\Delta G^{LX}$ for crystallization is calculated to be very small indicating a good glass forming ability of these alloys.

The analysis employed in the present work is quite general and can be applied to other kinds of glasses. Furthermore, the knowledge of the parameters such as the configurational entropy and the Gibb's free energy differences obtained from such studies should also be useful from the point of view of testing various models for glasses.
References


