Chapter 4

Theoretical investigations on the glass-forming ability of Zr-based metallic glasses

4.1 Introduction

The discovery of new metallic glasses and bulk metallic glasses (BMGs) have become very important due to their excellent properties and promising applications in various fields [176–179] After the fabrication of the first metallic glass $Au_{75}Si_{25}$ [12] in 1960, a variety of the BMG families of Zr-[180], Fe-[181], Cu-[182], Pd-[13], Mg-[183], La-[184] and Ti-[185] based multicomponent systems have been found. Out of these BMGs, Zr-based BMGs have drawn a lot of attention owing to its high GFA [180], [186–189]. The best glass-formers can be predicted by their GFA which is defined as the ability of a liquid melt to avoid the crystallization during the glass-formation process [190]. Inoue [168], in 1998, proposed three empirical rules to predict better GFA. These rules mainly involve three factors namely, the number of elements in the alloys, atomic size mismatch and heat of mixing. It suggests that three or more elements with atomic size mismatch > 12% and negative heat of mixing between the main elements should be a prerequisite for an alloy to be a good

glass former. These factors are most often interrelated and govern the thermodynamic behavior as well as the stability of the alloys against crystallization in the supercooled region.

It is well-known fact that the mixing of solute atoms with significantly different sizes compared to the atoms of the host element leads to the formation of local atomic clusters with five-fold symmetry which is incompatible with the three-dimensional packing. The resultant geometrical frustration promotes glass formation in an alloy. However, the presence of impurity atoms such as carbon, oxygen etc. adversely affects the GFA of an alloy. In case of mixing of rare-earth/transition metal elements, a large amount of charge transfer occurs due to the difference in their electronegativity. The doping of rare-earth elements also helps to remove the impurities to yield better GFA [191]. Therefore, the concentration of rare-earth elements in transition metal-based multicomponent alloy plays a dominant role in controlling the fundamental factors like the atomic packing and heat of mixing that affect GFA [192–194]. Thus, the study of the thermodynamics of alloys in the supercooled region can provide a better understanding of the science behind glass formation [170]. Experimental investigation of the thermodynamics of glass-forming systems is a challenging task due to the metastable nature of the supercooled liquid state. Nevertheless, calorimetric experiments on the metallic glasses yield information on the glass transition temperature (T_g) and the onset crystallization temperature (T_x). The difference, $\Delta T = T_x - T_g$, is considered to be a measure of the width of the supercooled region which is correlated to GFA. Higher ΔT_x corresponds to higher GFA and greater thermal stability [195]. However, a detailed investigation of the kinetics of nucleation and growth process in the supercooled liquid region requires the knowledge of the Gibbs free energy difference (ΔG) between the supercooled liquid state and the corresponding crystalline state. ΔG can be obtained experimentally through specific heat measurements. The drastic dynamics slow down and the thermal instability constrain the specific heat measurements in the limited temperature range in the vicinity of the melting temperature (T_m) and T_g. The only

alternative for the estimation of ΔG in a wide supercooled region is to use different analytical expressions which have been proposed over the years [98–107].

In the present work, Zr-based BMG alloy $Zr_{56-x}Co_{28}Al_{16}Y_x$ (x = 0, 2, 7, 10 at. %) has been investigated to study the effect of yttrium (Y) doping on its thermodynamics in the supercooled region. An experimental approach [196] that gives an excellent estimate of the temperature dependence of important thermodynamic quantities (ΔC_p, ΔH, ΔS and ΔG) in a wide supercooled region for a variety of BMG forming alloys has utilized. The results obtained provide useful insight into the effect of the factors such as the atomic size mismatch, electronegativity on the GFA of the investigated alloy.

4.2 Theoretical Formulation

The theoretical formalism begins with the basic equations of thermodynamics where the Gibbs free energy difference (ΔG) between the liquid and the crystalline phases can be expressed as

$$\Delta G = \Delta H - T\Delta S \tag{4.1}$$

where

$$\Delta H = \Delta H_m - \int_T^{T_m} \Delta C_p dT \tag{4.2}$$

$$\Delta S = \Delta S_m - \int_T^{T_m} \Delta C_p \frac{dT}{T} \tag{4.3}$$

ΔH_m and ΔS_m are the difference in enthalpy and entropy at T_m and both are correlated as the following equation:

$$\Delta S_m = \frac{\Delta H_m}{T_m} \tag{4.4}$$

ΔC_p, which is the difference in the specific heats of both the phases [191], can be given as

$$\Delta C_p = C_p^l - C_p^x \tag{4.5}$$

$$C_p^l(T) = 3R + cT + dT^{-2} \tag{4.6}$$

$$C_p^x(T) = 3R + aT + bT^2 \tag{4.7}$$

Here, a, b, c and d are the fitting parameters [191] and R=8.3142 J/g atom K.

Since, ΔC_p is difficult to obtain experimentally, the approximations in Eqs. (4.6) and (4.7) are substituted in Eq. (4.5) to get ΔC_p. It is subsequently used in Eqs. (4.2) and (4.3) and simplified analytical expressions are derived as given below:

$$\Delta H = \Delta H_m - \Delta T\left[\frac{(c-a)}{2}(T_m + T) - \frac{b}{3}(T_m^2 + T^2 + T_m T) + \frac{d}{T_m T}\right] \tag{4.8}$$

$$\Delta S = \Delta S_m - \Delta T\left[(c-a) - \frac{(T_m + T)}{2}\left(b - \frac{d}{T_m^2 T^2}\right)\right] \tag{4.9}$$

ΔG can be calculated by using different approximations for the temperature dependence of ΔC_p. In this study, an expression derived by Dhurandhar et al [107] has been utilized which is given as

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m} - \Delta C_p^m T_m\left[\ln\left(\frac{T_m}{T}\right) - \frac{\Delta T}{T_m}\right] \tag{4.10}$$

where, $\Delta T = T_m - T$

To deduce Eq. (4.9), hyperbolic variation of ΔC_p has been assumed. So far, numerous expressions describing ΔG have been derived [98–107] which exhibit a relatively small supercooled liquid region (SLR) for which the logarithmic term "$\ln(T_m/T)$" is approximated by using Taylor series expansion up to first two terms [107]. But it limits the validity of the expression for ΔG to a small SLR as it highly deviates from the experimental results. Parallelly, ΔH and ΔS have also been calculated theoretically by integrating Eqs. (4.2) and (4.3) respectively where,

$$\Delta C_p = \frac{\Delta C_p^m T_m}{T} \tag{4.11}$$

Substituting Eq. (4.11) in Eqs. (4.2) and (4.3), ΔH and ΔS take the forms as expressed below:

$$\Delta H = \Delta H_m - \Delta C_p^m T_m \ln\left(\frac{T_m}{T}\right) \tag{4.12}$$

$$\Delta S = \Delta S_m + \Delta C_p^m T_m \left[\frac{1}{T_m} - \frac{1}{T}\right] \tag{4.13}$$

Eqs. (4.12) and (4.13) provide an estimation of ΔH and ΔS in the SLR. These quantities can often be useful for the prediction of thermodynamic and kinetic parameters such as Kauzmann temperature (T_K) and the fragility parameter m. The Kauzmann temperature is defined as a lower limit of T_g and is also known as the ideal glass transition temperature at which the entropy difference ΔS vanishes. Thus, at $T = T_K$, $\Delta S = 0$, and Eq. (4.13) becomes

$$T_K = T_m \left(1 + \frac{\Delta S_m}{\Delta C_p^m}\right)^{-1} \tag{4.14}$$

By calculating T_K, the preliminary data of thermodynamic parameters could be easily obtained through experiments. However, more accurate empirical equations have been proposed for the estimation of T_K based on a detailed analytical treatment involving the fragility parameter m [197, 198]. The empirical expressions derived by Wang et al [107] for m and T_K are given by

$$T_K = T_m \left(1 + \frac{\Delta H_m}{T_g \Delta C_p^{l-c}(T_g)}\right)^{-1} \tag{4.15}$$

$$m = \Lambda_b \frac{\Delta C_p^{l-c}(T_g)}{\Delta S_m} \tag{4.16}$$

where, Λ_b is a constant with its value being 43. Defining $T_m/T_g = \Lambda_c$ and using Eqs. (4.4) and (4.16) become [198]

$$m = \Lambda_b \Lambda_c T_g \frac{\Delta C_p^{l-c}(T_g)}{\Delta H_m} \tag{4.17}$$

It has been observed that the empirical relation, $\frac{T_m}{T_g} = \frac{3}{2}$ holds for most of the glass-forming liquids. Using Eq. (4.17) in Eq. (4.15), T_K can be related to m by the following relation:

$$T_K = \Lambda_c T_g \left(\frac{m}{m + \Lambda_b \Lambda_c}\right) \tag{4.18}$$

4.3 Results and Discussion

All the thermodynamic quantities discussed in the previous section for all the mentioned compositions of the $Zr_{56-x}Co_{28}Al_{16}Y_x$ (x = 0, 2, 7, 10 at. %) BMG have been calculated theoretically and the results have been compared with the experimental results which are shown in Figs. 4.1-4.16. The input parameters necessary for calculations are taken from Ref. [191] and given in Table: 4.1.

Table 4.1: Parameters used to calculate ΔG and ΔC_p for $Zr_{56-x}Co_{28}Al_{16}Y_x$ alloys (Ref. [191]).

Y (at%)	T_g (K)	a (10^{-3}) (J/molK^2)	b (10^{-6}) (J/molK^2)	c (10^{-2})	d 10^6 (J/molK^2)	ΔH_m (kJ/mol)	ΔS_m (J/mol K)
0	742	1.126	8.1604	1.86	8.1705	12.842	11.285
2	731	1.048	1.7009	0.51	4.6112	10.531	9.238
7	724	1.546	1.80881	0.68	5.4213	9.524	8.391
10	714	2.306	2.6163	0.66	2.4309	8.084	7.154

The temperature dependence of Gibbs free energy difference (ΔG) in the alloy with different Y concentrations has been obtained using Eq. (4.10) and shown in Figs. 4.1-4.4.

Our results are, in general, excellent agreement with the experimental results in the entire supercooled region up to T_g. It substantiates the validity of Eq. (4.10) for the estimation of (ΔG). To understand the effect of Y concentration on (ΔG), we compare its values at experimentally reported values of T_g for these alloys [191]. For Y concentration of 0, 2, 7 and 10 at. %, the (ΔG) values at T_g are found to be 3.08, 3.18, 2.65 and 2.69 kJ/mol respectively. It is evident that the values of ΔG for the alloys with 7% and 10 at% of Y (with critical casting diameters $>$ 14 mm) are significantly lower than the values for the alloys with 0 and 2 at. % of Y and critical casting diameter of $\sim$ 6 mm. This demonstrates that lower ΔG corresponds to greater GFA.

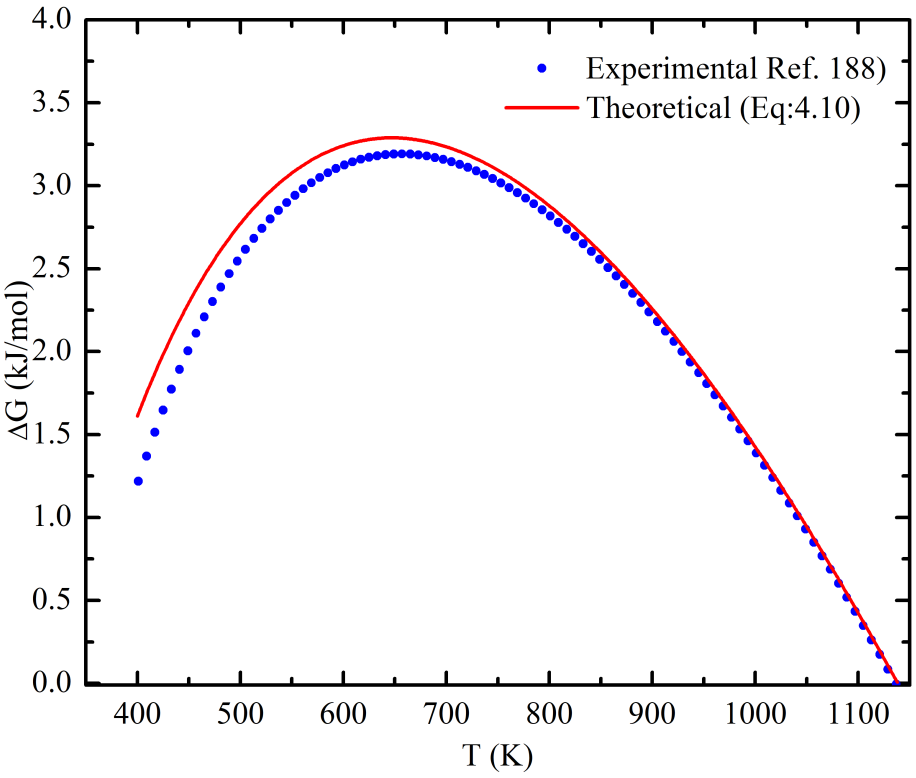

Figure 4.1: Gibbs free energy difference ΔG for $Zr_{56}Co_{28}Al_{16}Y_0$

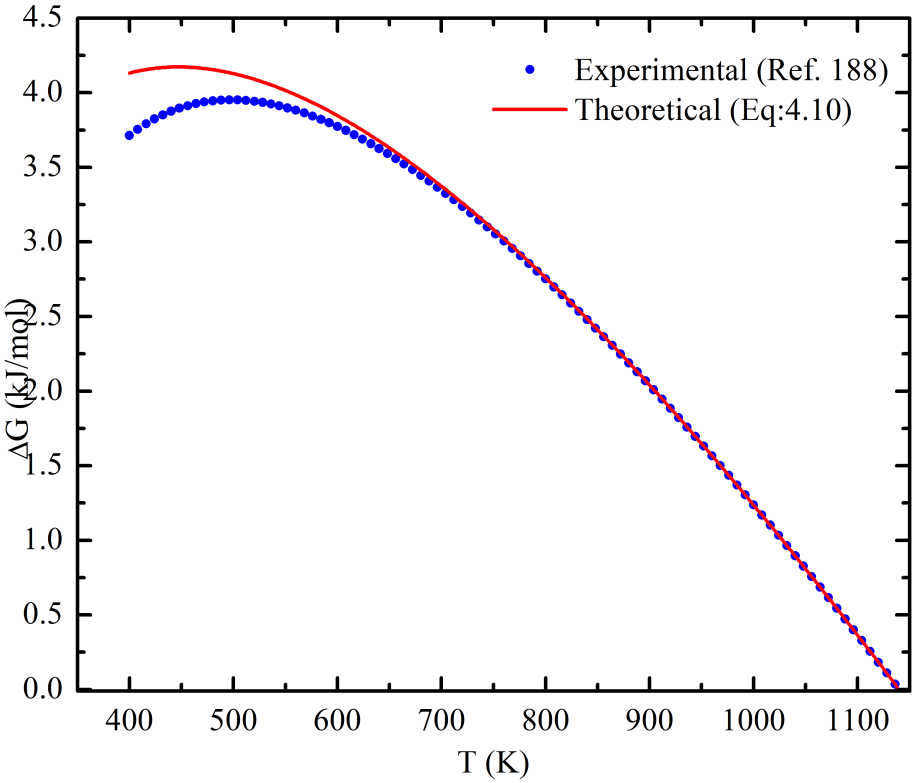

Figure 4.2: Gibbs free energy difference ΔG for $Zr_{54}Co_{28}Al_{16}Y_2$

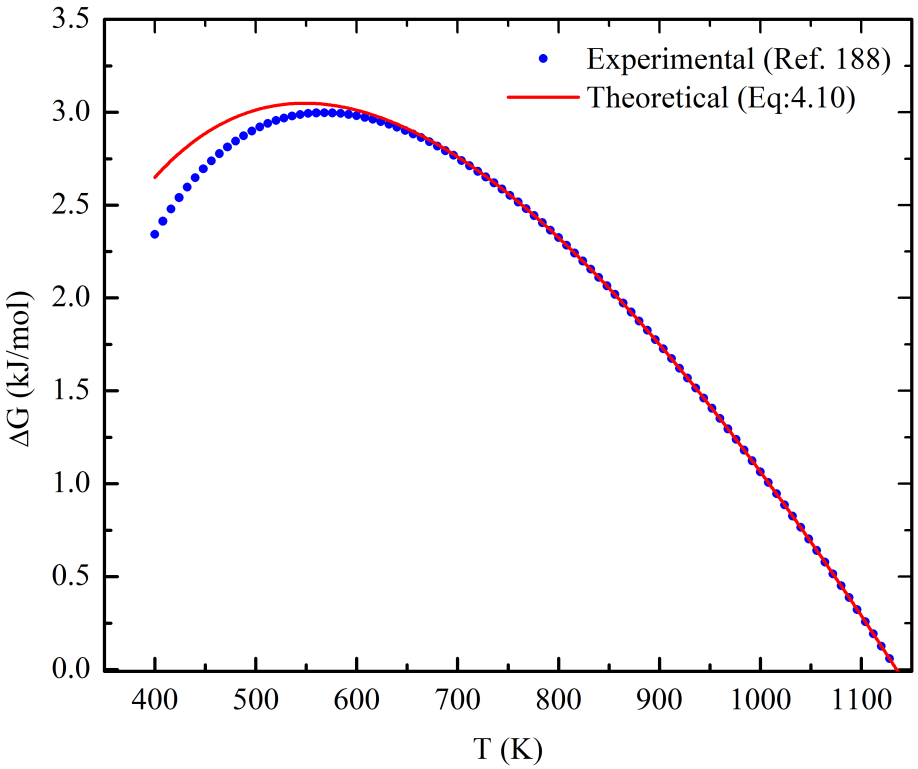

Figure 4.3: Gibbs free energy difference ΔG for $Zr_{54}Co_{28}Al_{16}Y_7$

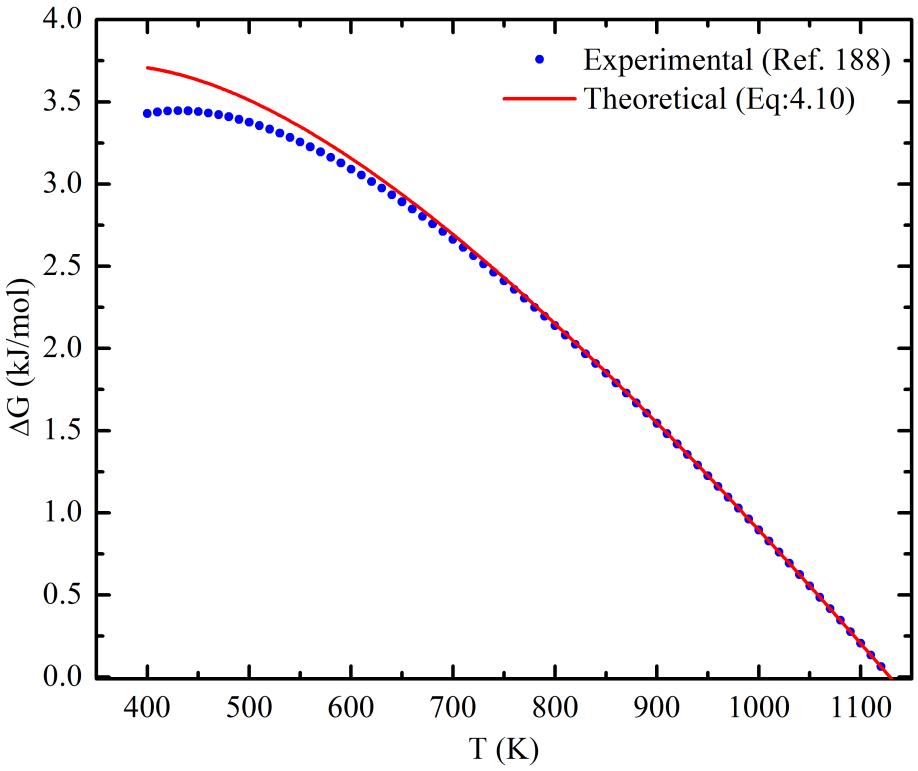

Figure 4.4: Gibbs free energy difference ΔG for $Zr_{54}Co_{28}Al_{16}Y_{10}$

Contrary to this, the kinetic parameters like T_g and ΔT_x do not show any direct correlation with GFA. Thus, the fundamental factors such as the atomic size mismatch, the heat of mixing that affect the thermodynamic behaviour of the alloys plays an important role in governing the GFA. Considering these factors, we get a plausible explanation for the observed GFA of the investigated alloys. The atomic sizes of Zr, Co, Al and Y are 206 pm, 152 pm, 118 pm and 212 pm, respectively. The heat of mixing for Zr-Co, Zr-Al, Co-Al, Co-Y and Al-Y are reported to be -41, -44, -19, -22 and -38 kJ/mol, respectively [199]. It can be easily observed that Y-Co and Y-Al have the highest atomic size mismatch of 28% and 44%, respectively. Also, the increase in the concentration of Y would result in larger negative heat of mixing of the alloy. These conditions, in accordance with the empirical rules mentioned earlier, explain the observed GFA of the studied alloys.

To understand the effect of electronegativity on the GFA, we evaluate a parameter, electronegativity difference using a model given by $\Delta x = \sqrt{\sum_{i=1}^{n} C_i(x_i - \bar{x})^2}$, [200] where x_i is the Pauling electronegativity for the i^{th} element of the alloy in the Pauling scale. Pauling electronegativities of Zr, Co, Al and Y are 1.33, 1.88, 1.61 and 1.22 respectively. Δx for the alloys with 0, 2, 7 and 10 at. % of Y are found to be 0.193, 0.242, 0.248 and 0.251, respectively. Though Δx increases with the increasing concentration of Y in the alloy, it does not show any direct correlation with the GFA. However, it is noteworthy that Δx values for the alloys with 2, 7 and 10 % of Y fall in the range 0.23 to 0.33 reported for 79 Zr-based BMGs [199]. Also, the Δx values for the alloys with 7 and 10% Y correspond to other Zr-based BMGs with critical cooling rates as low as 1.4 K/s [187].

To assess the difference in the temperature dependence of experimental ΔC_p and that obtained using hyperbolic approximation [(Eq. 4.11)], we plot both the results as shown in Figs. 4.5-4.8 for all the alloy compositions.

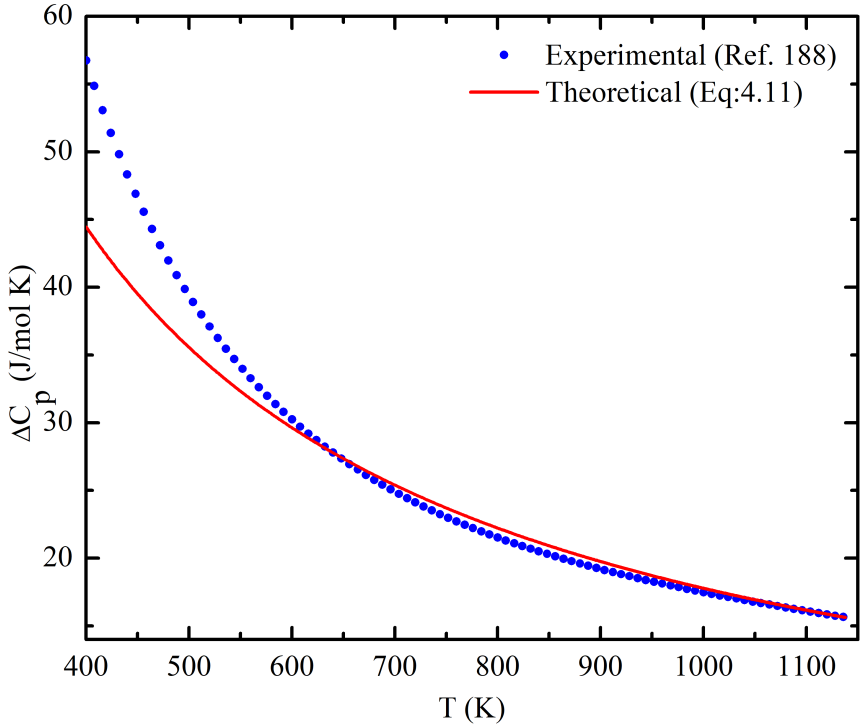

Figure 4.5: Specific heat capacity difference ΔC_p for $Zr_{54}Co_{28}Al_{16}Y_0$

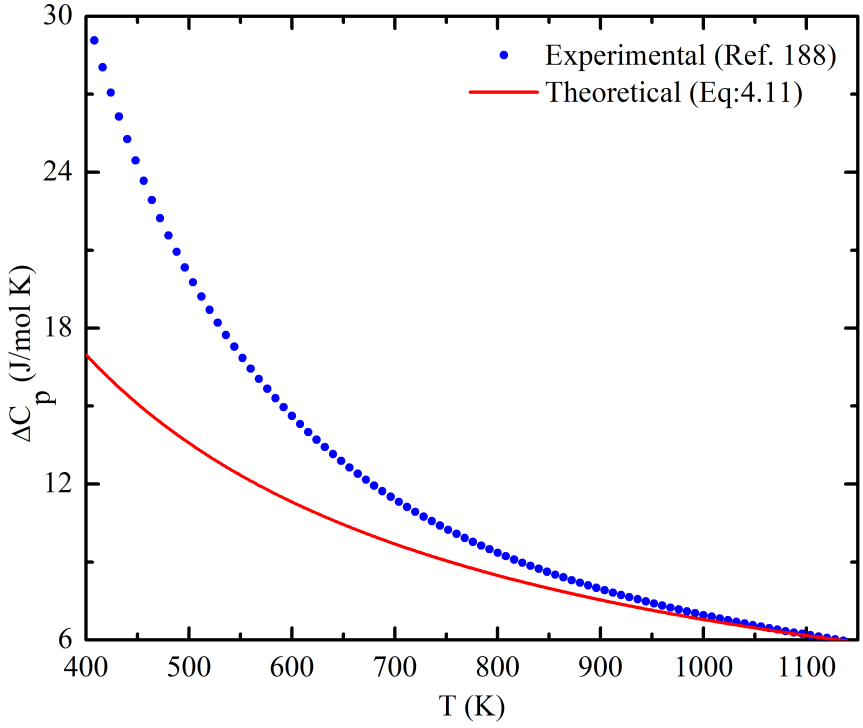

Figure 4.6: Specific heat capacity difference ΔC_p for $Zr_{54}Co_{28}Al_{16}Y_2$

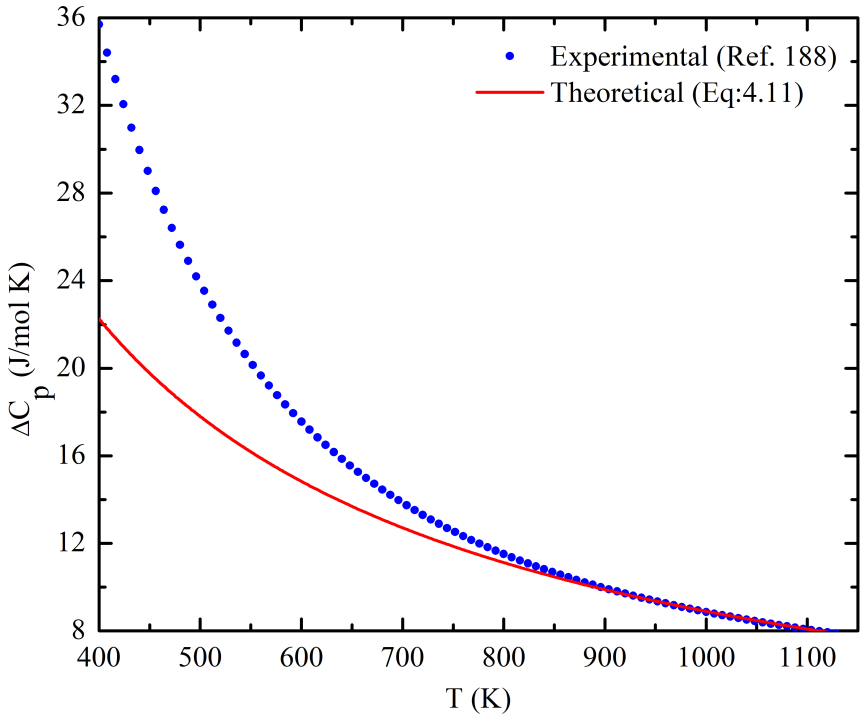

Figure 4.7: Specific heat capacity difference ΔC_p for $Zr_{54}Co_{28}Al_{16}Y_7$

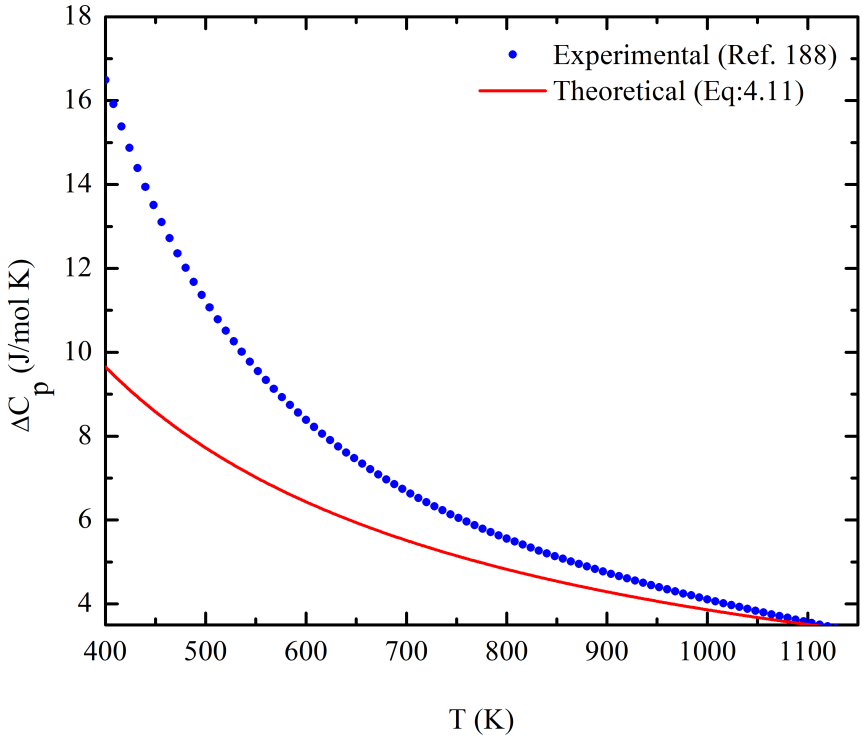

Figure 4.8: Specific heat capacity difference ΔC_p for $Zr_{54}Co_{28}Al_{16}Y_{10}$

Table 4.2: Fragility parameter (m) and Kauzmann temperature (T_K) estimated using Eq. 4.17 and 4.18, respectively. $\Delta_p^{l-c}(T_g)$ obtained using its temperature dependence given experimentally (Eq. 4.5) and the approximation (Eq.4.12)

Y	m		T_K (K)		
(at%)	Exp.	Theory	Exp.*	Theory	Theory Eq. 4.14
0	87	85	639	633	660
2	48	42	467	430	447
7	65	60	544	525	548
10	37	31	391	346	365

*Experimentally T_K is determined by extrapolating the heating rate dependence of T_g.

It can be observed that the temperature dependence of ΔC_p in both cases is quite similar, especially in the low supercooling region. The quantitative agreement of the approximated ΔC_p with the experiment decreases significantly for large supercooling. Although it might seem to be a matter of concern, it should be noted that the present hyperbolic approximation is far superior to the most commonly used linear temperature dependence of ΔC_p. The approximation of ΔC_p used in the present, in general, works well in the practically important temperature range i.e., T_m to T_g. This is also demonstrated quite clearly in the results of ΔH (Fig.: 4.9-4.12) and ΔS (Fig.: 4.13-4.16) obtained using the approximation. ΔH and ΔS are also useful for the determination of important parameters m and T_K.

The values derived using Eqs. (4.14), (4.17) and (4.18) are listed in Table: 4.2. The necessary values of $\Delta C_p^{l-c}(T_g)$ are obtained using Eq. (4.11) (theoretical) and Eq. (4.5) (experimental). It can be observed that the values of m and T_K are in reasonably close agreement with the experimentally extrapolated values. Surprisingly, T_K values obtained using our simple expression (Eq. 4.14), which relies on the thermodynamic parameters at T_m only, are also significantly closer to the values obtained using Eq. (4.18).

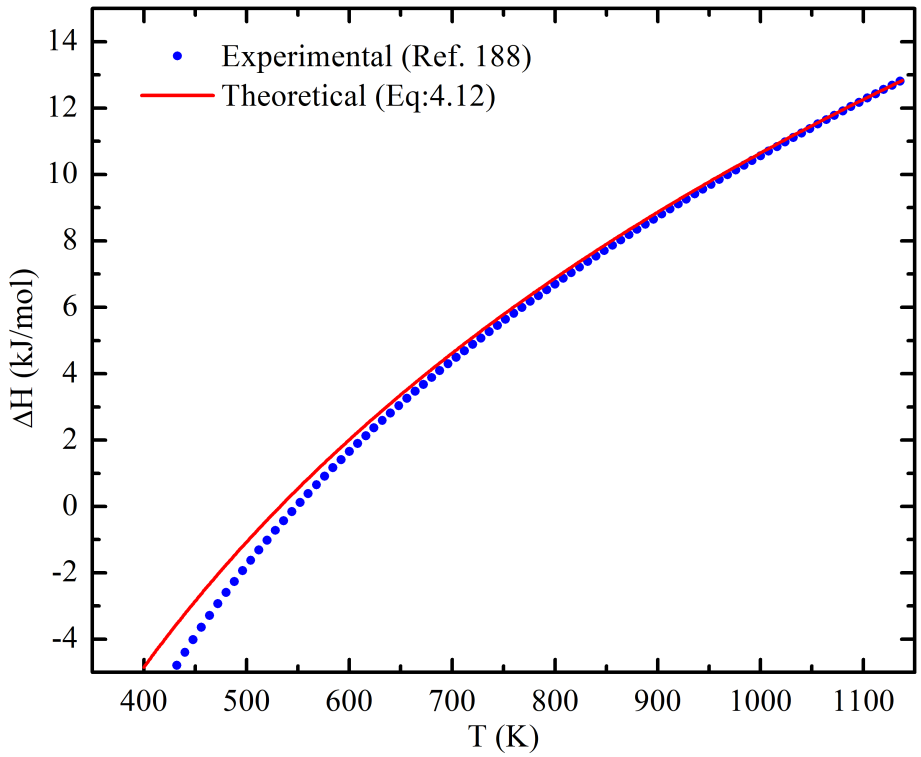

Figure 4.9: Enthalpy difference ΔH for $Zr_{54}Co_{28}Al_{16}Y_0$

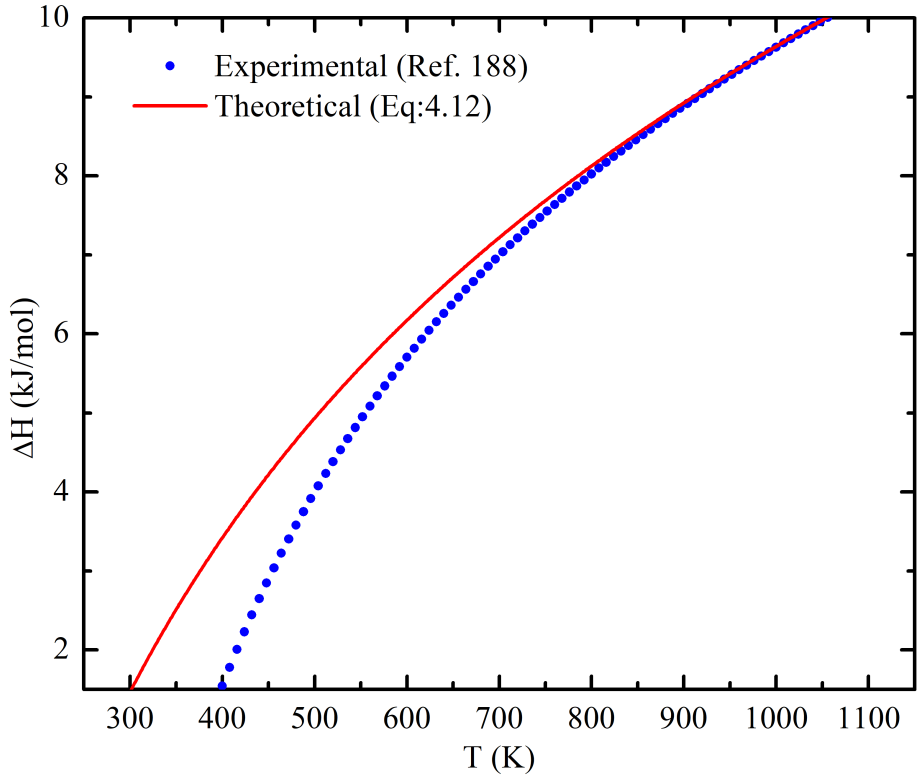

Figure 4.10: Enthalpy difference ΔH for $Zr_{54}Co_{28}Al_{16}Y_2$

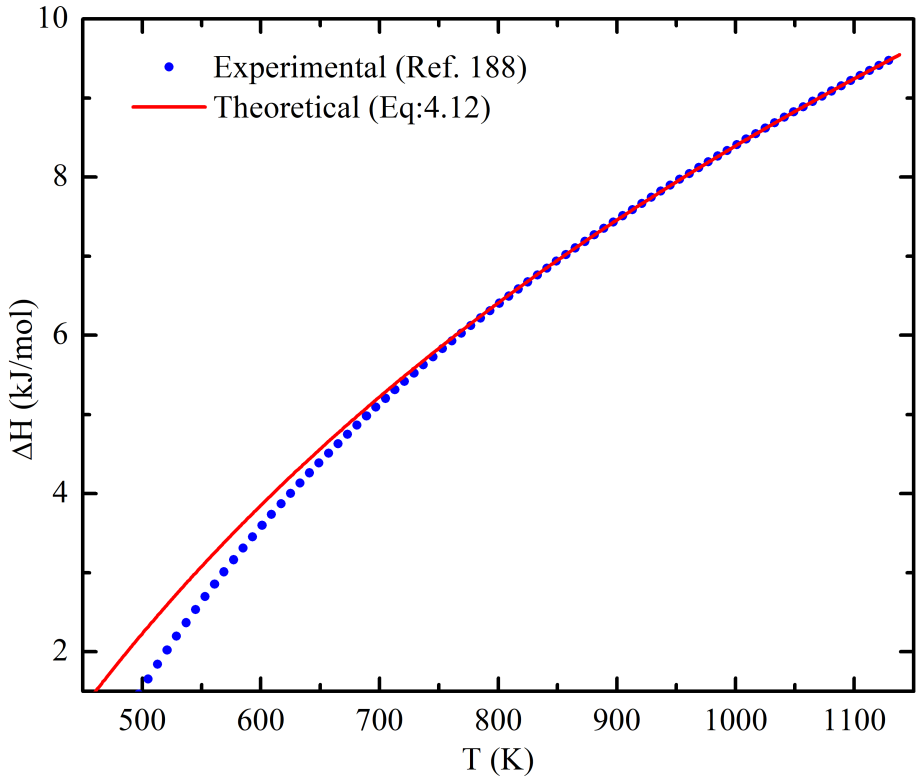

Figure 4.11: Enthalpy difference ΔH for $Zr_{54}Co_{28}Al_{16}Y_7$

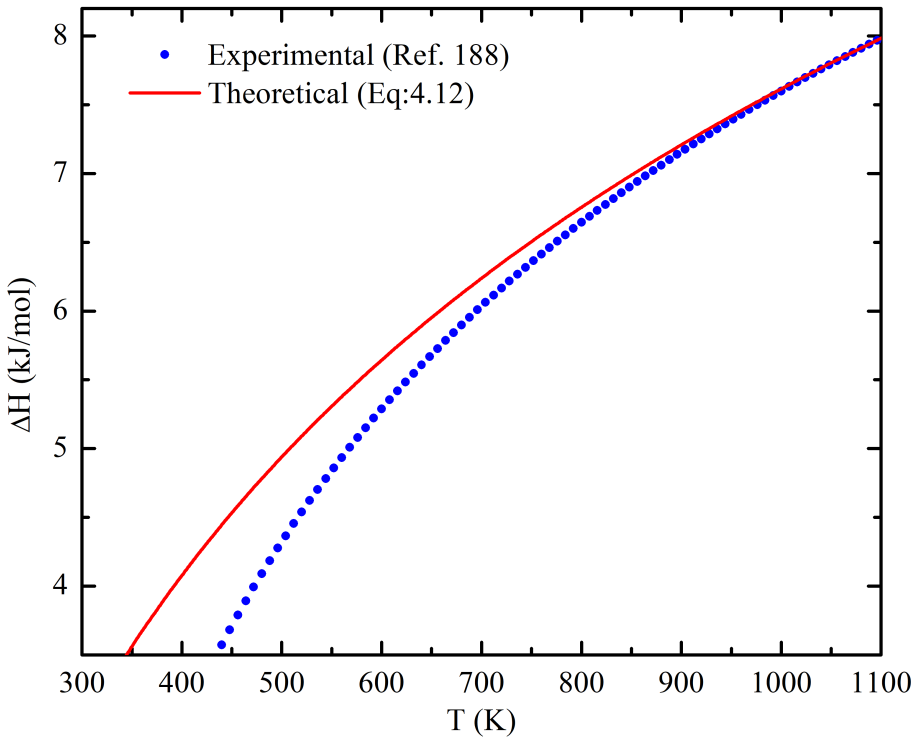

Figure 4.12: Enthalpy difference ΔH for $Zr_{54}Co_{28}Al_{16}Y_{10}$

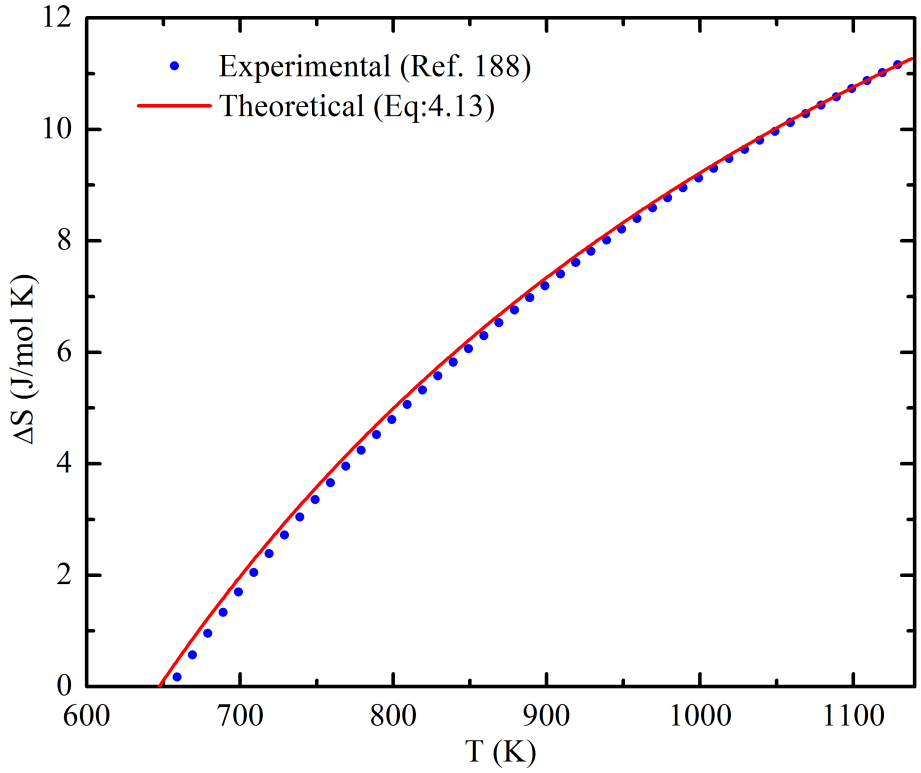

Figure 4.13: Entropy difference ΔS for $Zr_{54}Co_{28}Al_{16}Y_0$

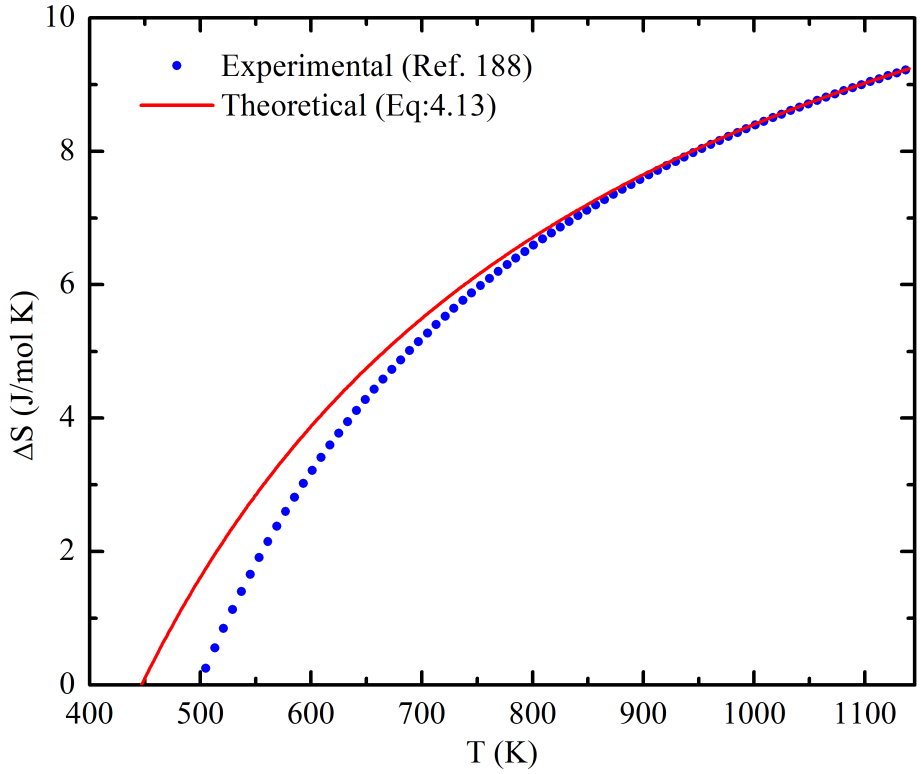

Figure 4.14: Entropy difference ΔS for $Zr_{54}Co_{28}Al_{16}Y_2$

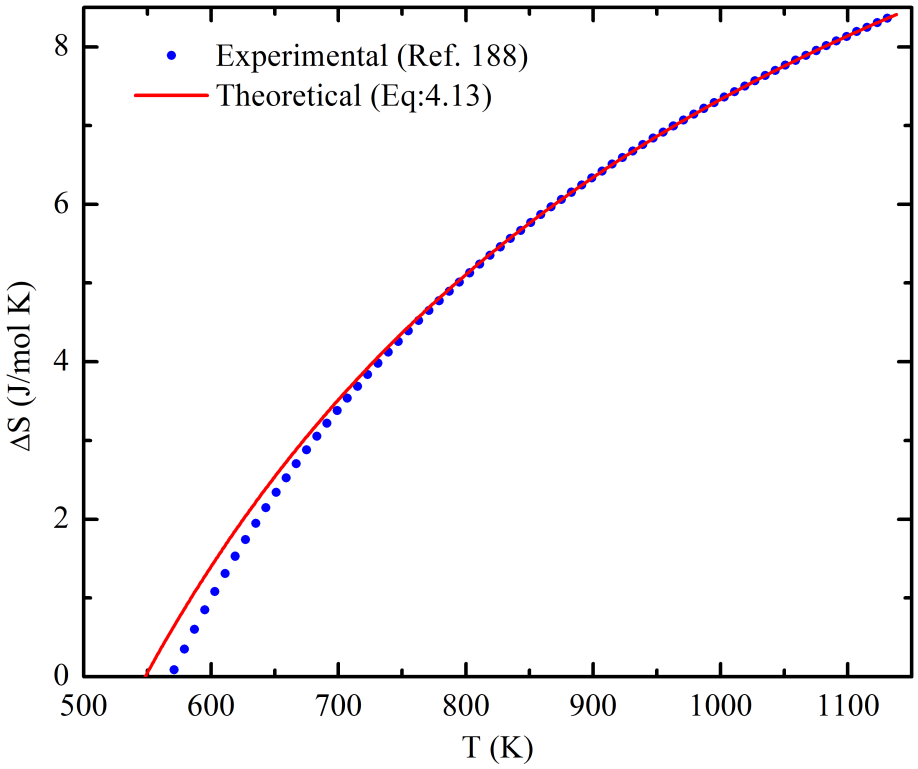

Figure 4.15: Entropy difference ΔS for $Zr_{54}Co_{28}Al_{16}Y_7$

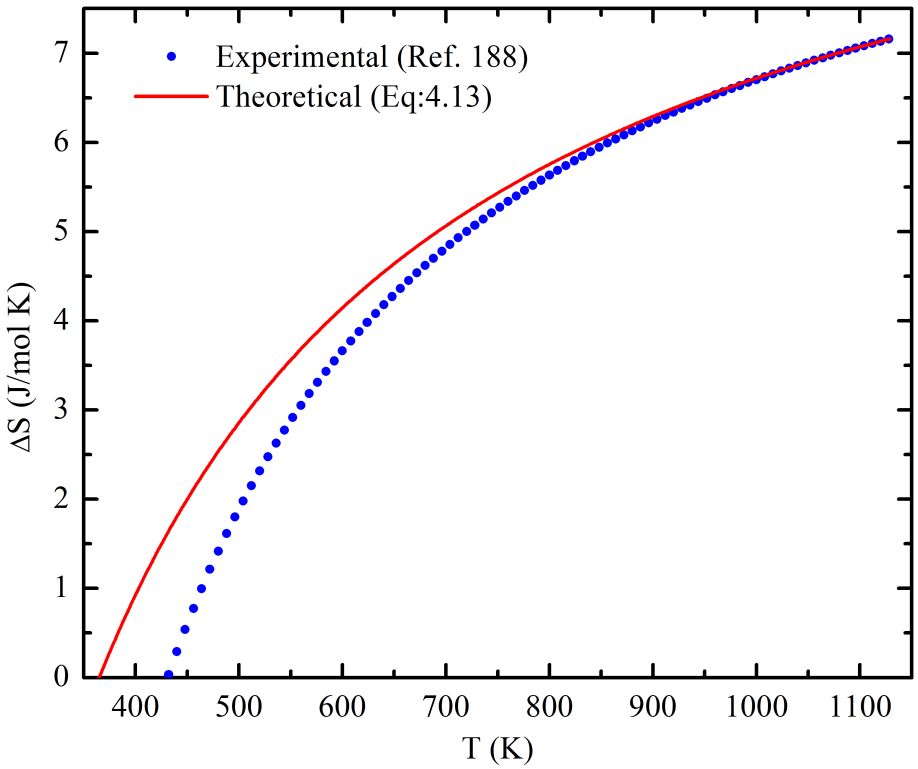

Figure 4.16: Entropy difference ΔS for $Zr_{54}Co_{28}Al_{16}Y_{10}$

Fragility parameters for most of the metallic glass-forming alloys fall in the range $30 \leq m \leq 70$ which corresponds to intermediate fragility [201]. Glass-forming liquids with $m < 30$ are considered to be strong and those with $m > 70$ as fragile [201]. In the present case, m for the alloy without Y is greater than 70. It indicates that this alloy is a fragile glass-former and its GFA is lower compared to the alloys with Y. The value of m for the alloy with 2 at% Y is much lower than the alloy with 7 at% Y which *prima facie* suggests the GFA of former to be greater than the later. Contrary to this, the critical diameter for the alloy with 7 at% Y (14 mm) is significantly higher than that for the alloy with 2 at% Y (5 mm). This inconsistency in the value of m can be attributed to its dependence on the thermal history of the alloy [197]. It is noteworthy that the alloy with 2 at% Y is produced by the copper mould-casting method whereas the alloy with 7 and 10 at% Y is produced using the water quench method [191].

4.4 Conclusion

The effect of Yttrium-doping in $Zr_{56}Co_{28}Al_{16}$ alloy on its thermodynamic behaviour in the supercooled liquid region has been studied using an analytical approach where the key thermodynamic quantities, ΔH, ΔS and ΔG, have been estimated theoretically using a hyperbolic approximation for the temperature dependence of the specific heat difference ΔC_p. Such an approximation is inevitable in the case of the non-availability of experimental data in the supercooled region. Temperature dependence of ΔG for $Zr_{56-x}Co_{28}Al_{16}Y_x$ (x = 0, 2, 7, 10 at. %) alloy in the supercooled region estimated using an analytical approach has been found to be in excellent agreement with the experimental results.

Present work sheds light on the influence of the fundamental elemental properties like atomic size, electronegativity, the heat of mixing, etc. on the investigated thermodynamic quantities. Amongst the Y doped alloys, ΔG for 7 and 10 at. % Y in the alloy has been found to be minimum and it signifies the observed high GFA

for these compositions. The low values of ΔG for these compositions could be attributed to the combined effect of the atomic size mismatch, negative heat of mixing and electronegativity difference.

As ΔG is correlated to the GFA of glass-forming alloys, the use of the present approach to estimate its value from preliminary thermodynamic data would enable the determination of an approximate doping concentration of an element in a multi-component alloy of interest. ΔH and ΔS estimation using the present approach can give useful first-hand information about the fragility parameter (m) and the Kauzmann temperature (T_K) for a given metallic glass-forming alloy.