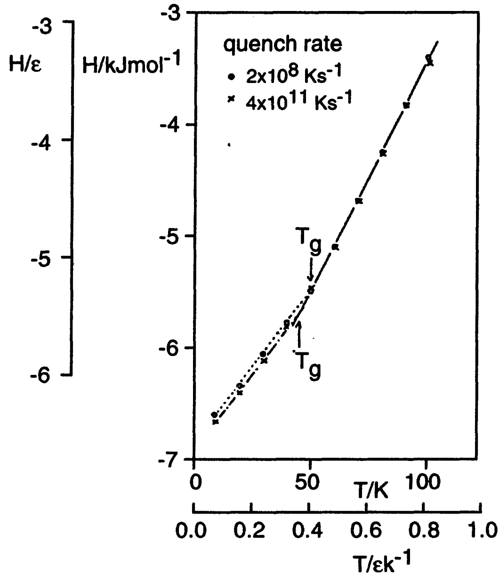

Figure 2.8. Entropy versus temperature curve for two cooling processes with the quenching rates of 2×10^{13} K/s and 4×10^{11} K/s (Yonezawa *et al.*, 1988).

2.3 Glass formation

Glass formation has been discussed for a long time from the viewpoints of thermodynamics, kinetics and structural properties (Kadoun, Chaussemy, Fornazero and Mackowski, 1983). In the case of glass formation by rapid quenching from the molten state of materials, the glass-forming ability is related to the viscosity of the melt. On cooling, viscous liquid does not provide the atomic mobility necessary for forming crystallites. Thus, when the viscosity is smaller, then glass formation becomes difficult. Indeed, the maximum glass-transition temperature in As_xSe_{1-x} is obtained for $x = 0.4$ and this composition almost corresponds to the maximum viscosity in the whole range of x. The glass-formation region as a function of x lies in $x < 0.57$ for As_xSe_{1-x} (see Fig. 2.9) and $x < 0.3$ for As_xS_{1-x}. These are also related to structural properties of As_xSe_{1-x} and As_xS_{1-x}. The threefold coordinated As atoms

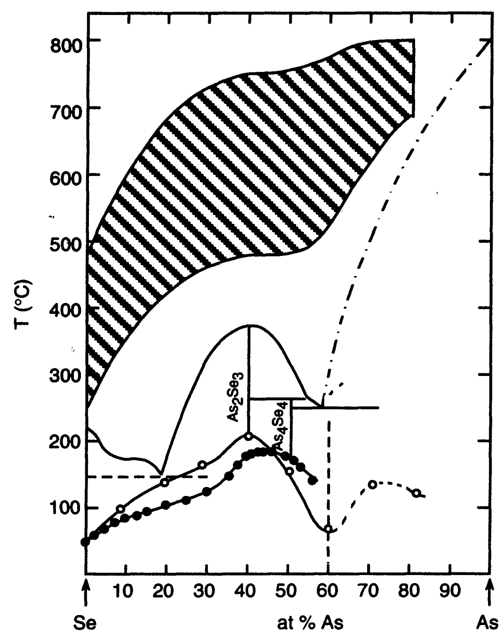

Figure 2.9. Phase diagram for the As-Se system (Kadoun *et al.*, 1983). Solid lines are from Myers and Felty (1967). The dashed zone is the range of viscosity measurements (see Kadoun *et al.*, 1983). The glass transition temperatures are given by the open and filled circles, which have been obtained by Mackowski (see Kadoun *et al.*, 1983) and Myers and Felty (1967).

play a cross-linking role in the chalcogen-chain network, so that as As atoms are added, the glass-forming ability becomes lower. Molecular species like As_4S_4 are formed when As concentration is increased. This also makes glass formation difficult, because the quasi-spherical molecule of As_4S_4 has insufficient steric constraints to prevent atomic movements necessary for crystallization on cooling (Elliott, 1991).

The glass-forming ability in chalcogenides has been discussed by Phillips (1979) in terms of a constraint model. He connected the glass-forming ability to steric constraints experienced by constituent atoms.

We consider a multicomponent system $A_xB_yC_z\dots$ $(x+y+z+\dots=1)$. The average coordination number m is given by

$$m = xn_c(A) + yn_c(B) + zn_c(C) + \dots, \tag{2.4}$$

where n_c is the coordination number of each atom. Each atom is constrained by its neighboring atoms through interatomic forces.

Phillips defines the number of constraints per atom, N_c, to be given by

$$N_c = \frac{m}{2} + \frac{m(m-1)}{2} = \frac{m^2}{2}, \quad (m \le N_d - 1), \tag{2.5}$$

where N_d is the number of available degrees of freedom. The first and second terms mean the freedom associated with a bond-stretching mode and the freedom associated with a bond-bending mode, i.e., the number of bond angles formed by two coordinated atoms, respectively. Equation (2.5) is valid for $m \le N_d - 1$, because the number of linearly-independent bond angles should be taken into account (Döhler, Dandoloff and Bilz, 1980). Thus, for $m \ge N_d - 1$ (Thorpe, 1983), N_c is given by

$$N_c = \frac{m}{2} + \frac{(N_d-1)(2m-N_d)}{2}, \quad (m \ge N_d - 1). \tag{2.6}$$

The ideal glass formation is obtained for $N_c = N_d$. Then, the optimum average coordination number is given by

$$m_c = \frac{N_d(N_d+1)}{2N_d-1}, \quad (m \geq N_d - 1). \tag{2.7}$$

For three-dimensional space, i.e. $N_d = 3$, we obtain $m = 2.4$ from Eq. (2.7). This means that the glass-forming ability is optimum for $m = 2.4$, namely, the network is overconstrained for $m > 2.4$ and is underconstrained for $m < 2.4$. This optimum average coordination number corresponds to As_2S_3 and As_2Se_3, i.e., the stoichiometric composition. As has already been mentioned, this is consistent with the experimental observation for the $As_xS_{1-x}(Se_{1-x})$ system. For the Ge_xSe_{1-x} system, the optimum composition obtained from Eq. (2.7) is $x = 0.2$, i.e., $GeSe_4$. This seems to correspond to a state of mechanical stability rather than chemical stability (i.e., $GeSe_2$) obtained from Eq. (2.7) (Elliott, 1991). For the Si_xO_{1-x} system, the optimum composition is $x = 0.2$. However, the stoichiometric composition is $x = 0.33$, i.e., SiO_2. Thorpe (1993) estimated the optimum composition to be $x = 0.33$ by neglecting the Si–O–Si bond angles, because the constraints associated with these bond angles are relatively weak.

Chalcogenide glasses containing I-group elements such as Cu and Ag have received much attention from structural viewpoints, i.e., the coordination number of I-group elements and their glass-forming ability (Liu and Taylor, 1989; Taylor, Saleh and Liu, 1990). Here we address the question of whether the I-group elements follow the $8 - N$ rule, i.e., the normal coordination rule. EXAFS measurements by Hunter *et al.* (1977) have shown that Cu is fourfold coordinated in amorphous $Cu_x(As_{0.4}Se_{0.6})_{1-x}$ with $x = 0.05$ and 0.25. This result is in contrast with the expectation from the $8-N$ rule, i.e., onefold coordination. Furthermore, glass formation is limited to below 30 at.% for Cu in the ternary Cu-As-Se system and for Ag in the ternary Ag-As-S(Se, Te) system, as shown in Fig. 2.10.

Liu and Taylor (1989) developed a general model to account for the above results and to describe the local structural order in multicomponent, covalent amorphous solids. Their so-called "formal valence shell" (FVS) model is based on the two major assumptions:

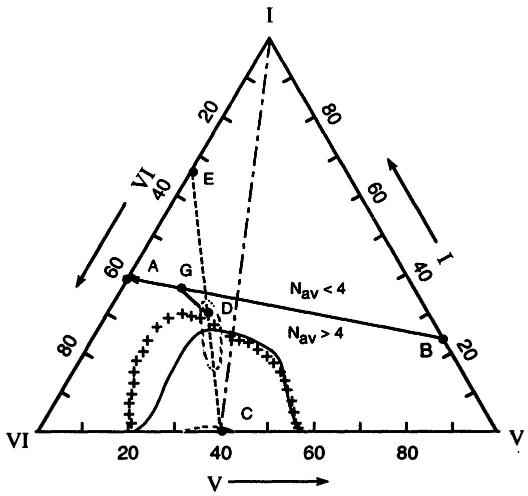

Figure 2.10. The glass formation regions for some I-V-VI systems: Cu-As-Se (solid curve), Ag-As-S (dotted curves) and Ag-As-Te(crosses). Specific points are shown as follows: (A) $I_{0.4}VI_{0.6}$; (B) $I_{0.25}V_{0.75}$; (C) $V_{0.4}VI_{0.6}$; (D) $I_{6/19}V_{4/19}VI_{9/19}$; (E) $I_{2/3}VI_{1/3}$; (G) $I_{3/8}V_{1/8}VI_{4/8}$ (see the text). Line AB shows the boundary ($N_{av} = 4$) between $N_{av} < 4$ and $N_{av} > 4$. The glass formation ($N_{av} = 4$) regions are within the region of $N_{av} > 4$ (Taylor *et al.*, 1990).

(1) The covalent nature of the interatomic bonding determines the nearest-neighbor coordination number; (2) All bonds are satisfied so that each atom formally obtains a closed shell of eight electrons. This means that, for example, when S(Se) or As atoms are bonded to Cu(Ag) atoms, nonbonding electrons are formally shared with Cu(Ag) atoms. The number of the valence electrons of each constituent atom is defined as N_f being generally not equal to N. Then, the coordination number Z is given by

$$Z = 8 - N_f\,. \tag{2.8}$$

Thus, the number of nonbonding electrons is equal to $N_f - Z$ which must be greater than or equal to zero. This restriction requires $Z \leq 4$ or $N_f \geq 4$. The formal transfer of nonbonding electrons occurs as mentioned above, in which the number of transferred electrons is minimized to obtain a stable configuration. When metal atoms ($N < 4$) are included, the above requirement leads us to their formal coordination number being equal to four.

Since every atom satisfies Eq. (2.8), the equation also holds on the average as follows: The average coordination number $Z_{\mathbf{av}}$ is given by

$$Z_{\mathbf{av}} = 8 - N_{\mathbf{av}} , \qquad (2.9)$$

where $N_{\mathbf{av}}$ is the average number of valence electrons.

In the following, we consider the glass-formation region in the $Cu_xAs_ySe_{1-x-y}$ system on the basis of the above consideration. Since $Z_{Cu} = 4$, $Z_{As} = 3$, $Z_{Se} = 2$, we have

$$N_{\mathbf{av}} = x + 5y + 6(1 - x - y) \qquad (2.10)$$

and

$$Z_{\mathbf{av}} = 8 - \{x + 5y + 6(1 - x - y)\} . \qquad (2.11)$$

Now, we assume that only the Cu-Se bond and As-Se bonds exist in the glassy $Cu_xAs_ySe_{1-x-y}$ system. Then, we have

$$Z_{\mathbf{av}} = 4x + 3y + (4x + 3y) . \qquad (2.12)$$

From Eqs. (2.11) and (2.12), we obtain

$$y = 0.4 - 0.6x . \qquad (2.13)$$

Thus, $Cu_xAs_{0.4-0.6x}Se_{0.6-0.4x}$ becomes the stable composition for the glassy Cu-As-Se system. For $x = 0$ and $x = 2/3$, we have As_2Se_3(point C in Fig. 2.10) and Cu_2Se (point E in Fig. 2.10), respectively. From Eqs. (2.12) and (2.13), $Z_{\mathbf{av}}$ and Z_{Se} are given by

$$Z_{\mathbf{av}} = 2.4 + 4.4x \qquad (2.14)$$

and

$$Z_{Se} = (1.2 + 2.2x)/(0.6 - 0.4x)\,. \tag{2.15}$$

Equation (2.15) shows that Z_{Se} increases from 2 with increasing x. From $Z_{Se} \leq 4$, we have a restriction of $x \leq 6/19$. A point corresponding to $x = 6/19$ shown as point D in Fig. 2.10 corresponds to the composition at which all Se atoms are fourfold coordinated. When the composition of Cu atoms further increases, then nonbonding electrons of As atoms are transferred into Cu atoms, so that As atoms change from the threefold coordinated state into fourfold coordinated. From a similar consideration to the above, we have a stable composition of $Cu_xAs_{(6-13x)/9}Se_{(3+4x)/9}$ for the glassy Cu-As-Se system. From $Z_{As} \leq 4$, we have a restriction of $x \leq 3/8$. The case of $x = 3/8$, shown as point G in Fig. 2.10, corresponds to the upper limit of x at which all As atoms are fourfold coordinated. From the above consideration, we have stable glassy compositions on the line C-D-G. As shown in Fig. 2.10, the glass-formation region of I-V-VI system (Cu-As-Se, Ag-As-S, Ag-As-Te) extends around the above line. This line corresponds to stoichiometric compositions for stable glassy systems. On the right side from the line C-D, we have As-As bonds, whereas on the left side from the line C-D, we have Se-Se bonds. The FVS model has been shown to be applicable to ternary glassy-forming systems (IV-VI-VII, IV-V-VI, II(III)-V-VI etc.).

The local order of atoms can be examined from nuclear quadrupole resonance (NQR). For example, from ^{75}As NQR measurements (Saleh, Williams and Taylor, 1989), the As-As bond percentage κ_4 has been estimated as a function of x in glassy $Cu_x(As_2Se_3)_{1-x}$ system, as shown in Fig. 2.11, where the average coordination number is also shown (Taylor, Saleh and Liu, 1990). The solid and dashed lines are those calculated from the FVS model. As seen in the figure, there is good agreement between theory and experiment.

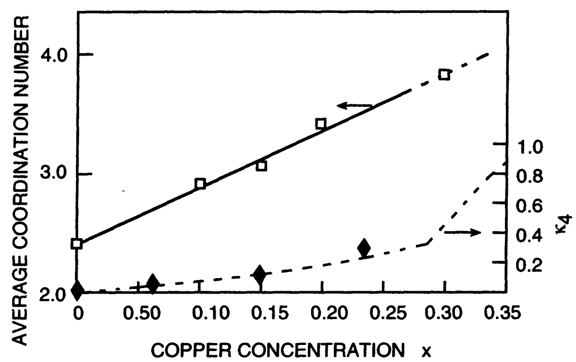

Figure 2.11. The average coordination number as a function of x in glassy $Cu_x(As_2Se_3)_{1-x}$ system. The As-As bond percentage κ_4 is also shown. The solid and dashed lines are the model calculation (Taylor *et al.*, 1990).