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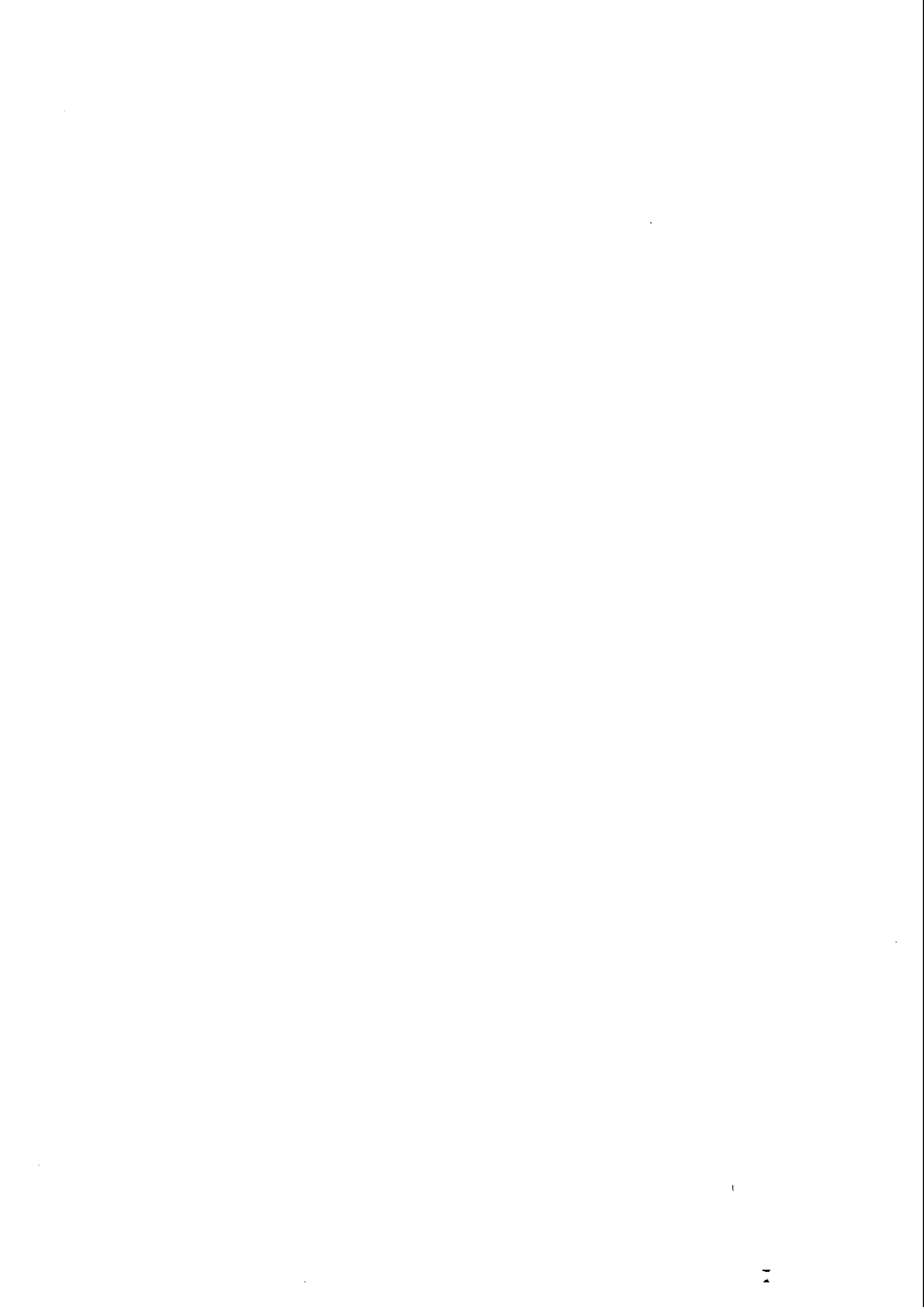International Centre for Theoretical Physics, Trieste, Italy.

ABSTRACT

Glass transition temperatures (T_g) and molar volumes (V), of 13 glassy compositions of the $Ge_{100-x}S_x$ system, were determined using differential scanning calorimetry (DSC) and the measured values of densities, respectively. The variation of T_g and V with the average coordination number, m, are examined in light of the models proposed for the structure of these covalently bonded solids.

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Recently, the variation with the average coordination number, of various physical, mechanical and thermal properties of multicomponent chalcogenide glasses has been a subject of intensive research [1-9].

The chemically ordered covalent network (COCN) model [10-13], and topological models such as the constraints model [14-17] and the structural transition model [18, 19], have been used in the interpretation of the compositional dependence of these properties. In the COCN model, wrong homopolar bonds are minimized, and the structure is assumed to be composed of three dimensional cross-linked structural units of the stable chemical compounds of the system. As a consequence of the chemical ordering, distinct features, e.g., a change in slope or extremum, at the stoichiometric or tie-line compositions (also known as chemical thresholds of the system [20]), are observed in the compositional dependence of the various properties.

The topological models are also employed to explain other distinct features observed in the property-composition dependence in network chalcogenide glasses. In these models, the properties are discussed in terms of the average coordination number which is indiscriminate to the species of the valence bond [19]. At $m \simeq 2.4$, the glass network has a mechanical or rigidity percolation threshold, at which the glassy network changes from floppy type to a rigid type. At $m = 2.67$, two dimensional layer structures are fully evolved and for $m > 2.67$ there is a structural transition to three dimensional structures due to cross-linking. The above mentioned topological thresholds have been observed in several systems [19]. As an example, in the variation of the molar volume with the average coordination number in $Ge - Se$ and $As - Se$ systems [21], the thresholds are marked by a minimum in V at $m \simeq 2.4$ and a maximum in V at $m \simeq 2.67$.

Molar volume results in $Ge_{100-x}S_x$ system have been reported by [22] and more recently by [23]. The small number of glass compositions examined [22] did not allow a resolution of anomalies in the compositional dependence of the various properties. The study of [23] revealed some anomalies, i.e. peaks in the compositional dependence of the molar volume at 25 and 34 at % Ge. However, no account of the variation of T_g and V with the average coordination number for this system, in the composition range covered in this study, to the best of the knowledge of the author, have been reported. In this paper the results of such a study are reported and discussed.

1 Experimental

The glasses, in the composition range $56 \leq x \leq 78$ (x in at %), were prepared by the conventional melt quenching method using crushed Ge and powdered S, both of high purity (99.999%). The method consisted of sealing, at a high pressure ($\sim 10^{-5}$ Torr), the weighted amounts of the constituent elements in a carefully outgased, argon flushed, rectangular-section silica ampoules ($1.5 \times 1.5 \times 6.0$ cm). The ampoules were then held, for 36 hours, in a rocking furnace in which they were heated gradually to a temperature of 900°C. At this temperature the liquid was completely homogeneous, and the ampoules were quenched to room temperature in a large volume water bath. For glasses with $x \geq 80$, the outlined procedure was used except that the samples were heated to a lower temperature (~ 750°C) and required only air cooling. The samples were X-rayed to confirm their amorphous nature.

A Perkin-Elmer DSC-2C differential scanning calorimeter using a scan rate of 20 K/min

and sample sizes of 15–20 mg of the powdered glass, was utilized to study the glass transition temperatures. The powdered samples were sealed in aluminium pan and compared with an empty aluminium pan. The measurements were performed in dried, oxygen free, nitrogen atmosphere. The glass transition temperature was taken at the midpoint of the step of the thermogram.

The ambient macroscopic densities of the virgin glasses were determined by the Archimedes method using ethyl–methyl–ketone as the immersion fluid, which has a density of 0.803–0.805 g cm^{-3} at 20°C. The molar volume of a given composition was determined by dividing the average molecular weight by its density.

2   Results and Discussion

Coordinations of 4 for Ge and 2 for S, obeying the so–called '8–N' rule [14, 24, 25], where N is the number of outer shell electrons, were used to calculate the average coordination number of the glasses examined. For a binary system $A_{1-x}B_x$, the average coordination number, m, is given by [26]:

$$m = (1 - x) \, N_C(A) + x \, N_C(B)$$

where $N_C(A)$ and $N_C(B)$ are the coordination numbers of atom A and atom B, respectively. The 'm' values obtained are listed in Table 1. The glass transition temperatures and molar volumes are also given in Table 1.

In the variation of V with m (Fig.1), a minimum in V at $m = 2.44$ and a maximum in V at $m = 2.67$ are observed. The minimum at $m = 2.44$ is attributed to the mechanical percolation threshold at which the transition from floppy type glass to a rigid type glass takes place. Phillips [14], by equating the number of degrees of freedom to the number of operative constraints, for the most stable glass, obtained an m value equal to 2.4. Thus the minimum in V at $m = 2.44$ is understood by assuming that the most stable glass should have a minimum in V [19]. The results of this work show that the observed threshold at $m = 2.44$ is slightly higher than the theoretical prediction of 2.4. This small systematic difference between the observed rigidity percolation threshold and the predicted one have been reported in amorphous $Ge_{100-x}Se_x$ from results of molar volume [21], steady–state photoconductivity [27], Raman scattering [28] and Mössbauer site–intensity ratio [29]. The results on a–$Ge_{100-x}Se_x$ system are supportive to our observation because $Ge - S$ and $Ge - Se$ are chemically similar families of chalcogenide glasses. The increase in V between $m = 2.44$ and $m = 2.67$ is attributed to an increase in the interlayer separation of the two dimensional structure proposed for the structure of chalcogenide glasses in this range of m. The maximum in V at $m = 2.67$ (corresponding to GeS_2 composition) is traced to the presence of pronounced intermediate range order (IRO) for this composition [30], which requires the widest interlayer separation. For $m > 2.67$ the transition to three dimensional structure is marked by a decrease in V. This reduction in V extrapolates to a value of V for a–Ge (at $m = 4$) equal to 15.762 cm^3. The density value obtained for a–Ge from this V value is 4.605 g cm^{-3}. Data also extrapolates to a value of V for $g - S$ (at $m = 2$) equal to 16.4 cm^3 which corresponds to a density value of 1.955 g cm^{-3}. The deduced densities are in close agreement with published values of 4.6 g cm^{-3} and 1.95 g cm^{-3} for the densities of a–Ge and $g - S$, respectively [31].

The $T_g - m$ dependence, when plotted from the data of Table 1, seem to consist of three regions (i) an initial region between $m = 2.2$ to 2.44 in which T_g varies slowly with m;

(ii) a region between $m = 2.44$ to $m = 2.67$ in which T_g changes steeply with m and finally (iii) a region in which T_g decreases for $m > 2.67$. Two features in $T_g - m$ dependence are seen. The first is a change in slope at $m = 2.44$ marking the transition from floppy type to rigid type glass and the second is a maximum at $m = 2.67$. It should be noted that, in glasses of this system (IV–VI elements) the chemical and topological thresholds coincide at $m = 2.67$, thus it is not possible to separate their effects. However, on an intuitive basis, the maximum in T_g at $m = 2.67$ is ascribed to a minimum in configurational entropy, a maximum in heteropolar bonding and hence to maximum chemical stability. Finally, the data in Fig.2 extrapolates at $m = 2$ to a value of T_g for $g - S$ equal to 249 K which is in good agreement with the published value of 246 K for T_g of $g - S$ [32].

3 Summary

In glasses of this system, a topological threshold at $m = 2.44$, slightly higher than the theoretical prediction at $m = 2.4$, is observed. At $m = 2.67$, both topological and chemical thresholds coincide and due to this fact it is not possible to separate their effects. For $m > 2.67$, the structural transition to three–dimensional network glass is marked by a decrease in both T_g and V.

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Table 1 Data of m, T_g and V for the glasses examined. T_g is in K; V in cm^3; and compositions are in at %.
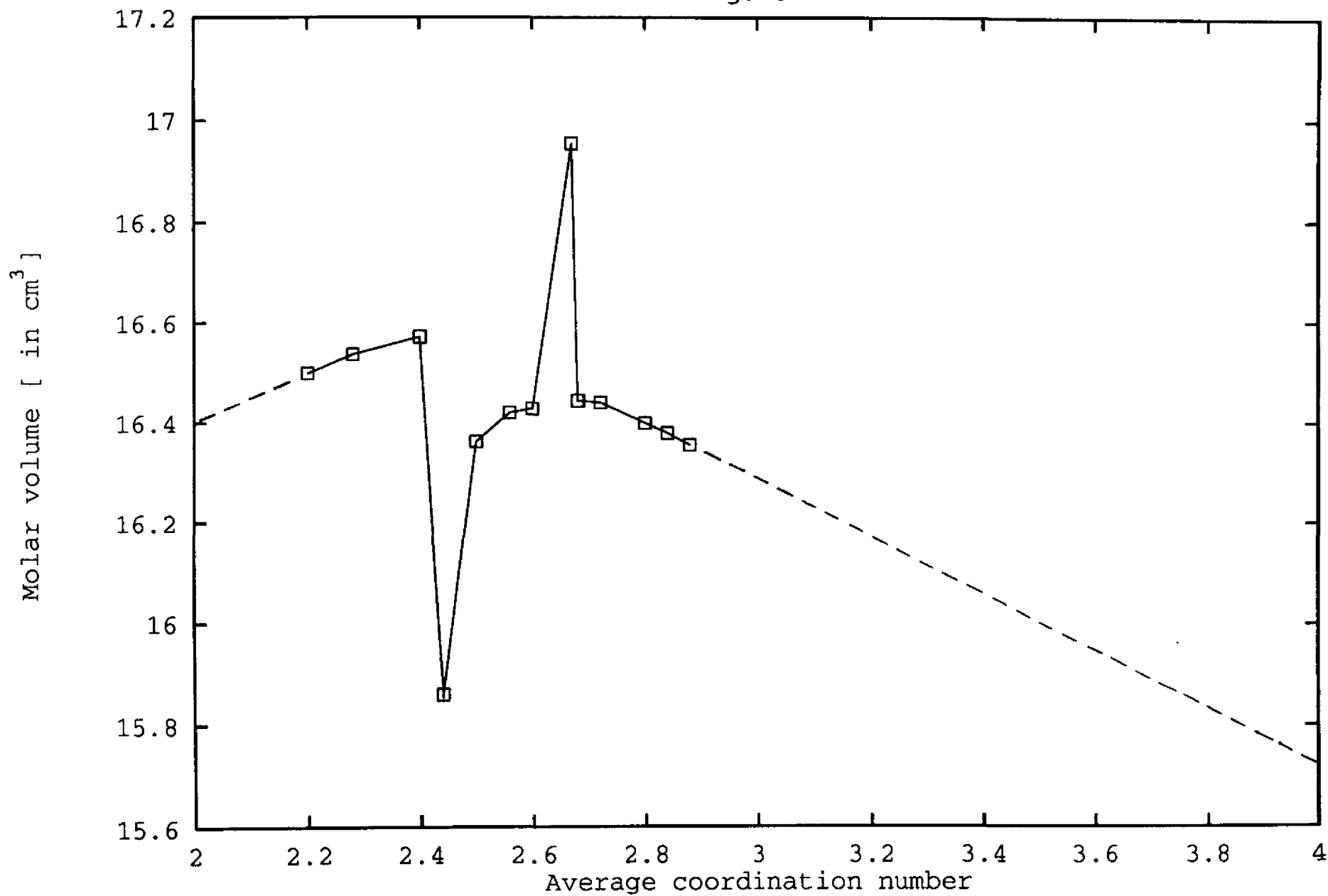
Table 1

Glass number	Ge at %	S at %	m	$T_g(K)$	$V(cm^3)$
1	10	90	2.2	290	16.499
2	14	86	2.28	307	16.537
3	20	80	2.4	331	16.571
4	22	78	2.44	340	15.859
5	25	75	2.5	412	16.361
6	28	72	2.56	486	16.419
7	30	70	2.6	550	16.427
8	33.33	67.67	2.67	762	16.954
9	34	66	2.68	735	16.443
10	36	64	2.72	703	16.439
11	40	60	2.8	653	16.398
12	42	58	2.84	631	16.378
13	44	56	2.88	625	16.354

FIGURE CAPTIONS

Fig.1 Variation of molar volume (V) with the average coordination number (m). Solid lines are drawn through data points as a guide for the eye.

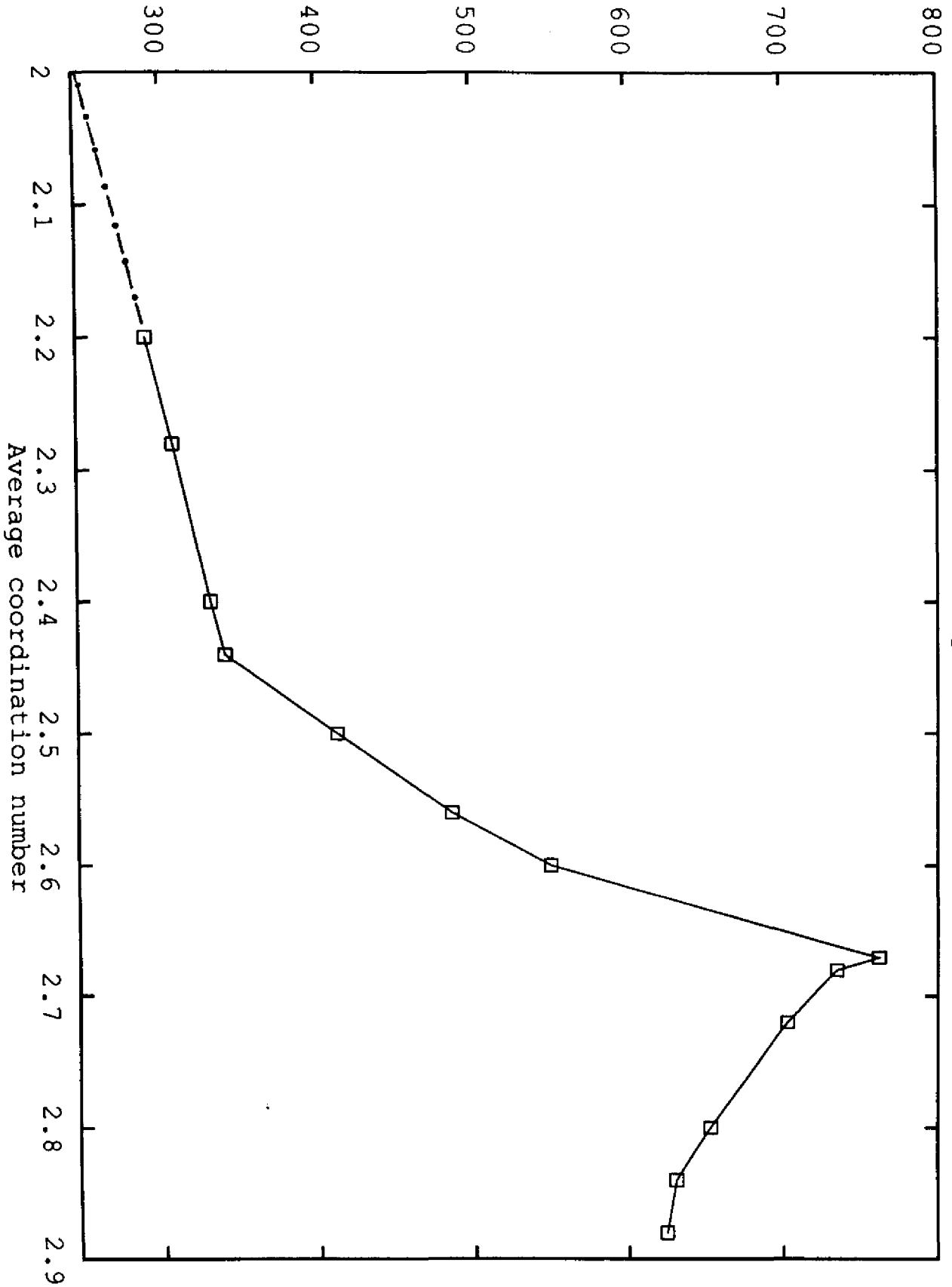Fig.2 Variation of glass transition temperature (T_g) with the average coordination number (m). Solid lines are drawn through data points to guide the eye.

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Figure 1

Figure 2