JOURNAL OF SOLID STATE CHEMISTRY 2, 182–187 (1970)

Atomic Distribution in the Glass Forming System Ge–As–Se

H. KREBS AND H. WELTE[†]

Technical University of Stuttgart, Institute for Inorganic Chemistry, Stuttgart, Germany

Received December 1, 1969

The atomic distribution curves of chalcogenide glasses with the compositions 1, $Ge_{30}Se_{70}$; 2, $Ge_{20}Se_{40}As_{40}$; 3, $Ge_{35}Se_{25}As_{40}$; and 4, $Ge_{45}Se_{25}As_{30}$ have been determined. The coordination numbers obtained for the first coordination sphere correspond to the weighted mean of Ge coordination number 4, As 3, and Se 2. Also the distance between nearest neighbours corresponds to the average of the calculatable covalent distances. The glass $Ge_{30}Se_{70}$ shows an atomic distribution which is similar but with larger distances to that expected for a smeared out GeS_2 lattice.

Introduction

The so-called chalcogenide glasses are being studied intensively because of their optical and electrical properties. They are also of very great interest from the scientific point of view because the general rules for the forming of glasses can be followed very easily. Moreover, a particular problem is involved, which cannot be explained with classical chemical ideas. With increasing atomic number, the valency electrons show an increasing tendency to form two-sided binding *p* states rather than one-sided binding hybrid states. Insulators first become semiconductors and finally metallic conductors. Therefore, it seemed important to determine the atomic short range order of suitable chalcogenide glasses.

Investigations of this kind have been performed mainly by Vaipolin (*1*) and Dobrott (*2*). The accuracy of these investigations is not satisfactory because the glasses which were used consisted of atoms of very different nuclear charges. Exact atomic distribution curves are obtained if the atoms forming the glass have similar atomic numbers because then the so-called atomic form factors differ only slightly.

We chose the ternary glass forming system Ge–As–Se for our investigations. This system is shown in Fig. 1. The full curve surrounds the area in which a glass forms by air quenching (*3–6*), the broken curve surrounds the area in which perfect glassy solidification is obtained only by water quenching (*7*). The points 1, 2, 3, and 4 signify the compositions of the samples investigated in this study.

Samples

According to the composition desired, elements of high purity were weighed in a quartz ampulla. The total weight was 20 g. The components were introduced into the ampulla in the order Se, As, and Ge. The ampulla was then evacuated, melt off and heated

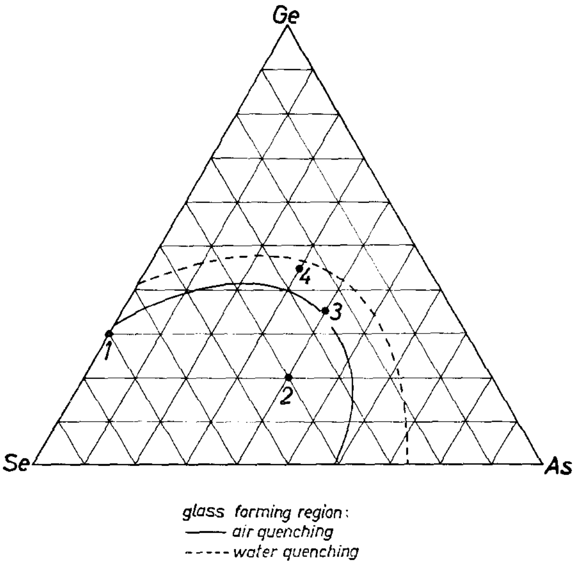

FIG. 1. Glass forming system Ge–As–Se. The points 1, 2, 3, and 4 indicate the composition of the samples investigated.

[†] Thesis, Stuttgart 1969.

vertically so that the As first of all sank in the molten Se and reacted. By this procedure the reactivity and the vapour pressure of the As were reduced so that further increase of temperature led to no vehement reactions combined with explosions. The free space above the melt was always kept hotter than the sample in order to avoid a sublimation of As. After cooling the ampulla was melted off directly above the regulus. In order to homogenize the sample, the shortened ampulla was then shaken constantly in the furnace at a temperature of 1000°C for 24 hr and subsequently quenched in water. The regulus was powdered and so sifted that only particles with a diameter of less than 20μ were used. Under addition of some acetone the powder was elutriated into a brass vessel so that a sample with an even surface was formed.

Measurements

The measurement of the intensity distribution was performed with a goniometer according to Bragg–Brentano already described (*8*). The X-ray tube of the goniometer and a holder on which a slit system, a monochromator, and a scintillation counter are fixed turn in opposite senses about an axis contained in the surface of the sample. The width of the blind was so chosen that the compton scattering over the whole angle enters the scintillation counter also. The corrections, calculation methods and normalisation procedures for the transformation of the intensity distribution into the atomic distribution curves were performed as described in (*8*) and (*9*).

Results and Interpretation

The measured intensities of the samples are reproduced in Fig. 2. Figures 3 and 4 show the corresponding normalization curves and the $F(s)$ curves. The $F(s)$-curves represent the essential part of the integrand in the Fourier transformation. Figures 3 and 4 show clearly that for the limit given by MoKα-rays, i.e., $s \approx 16$, intensity changes are still observed. From this one can conclude to a high

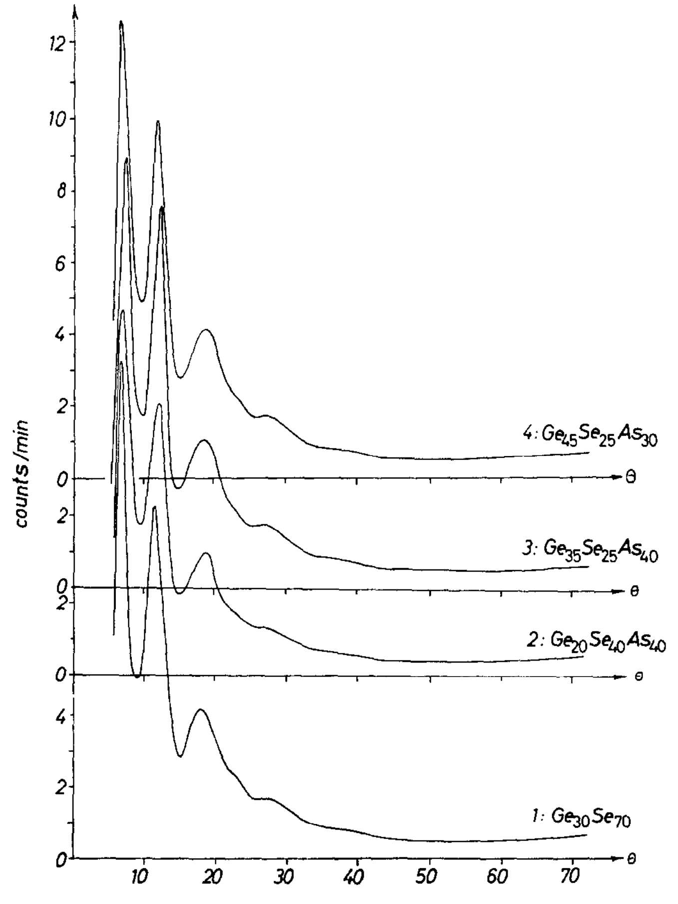

FIG. 2. Measured intensity curves. Impulses per minute (relative) versus θ.

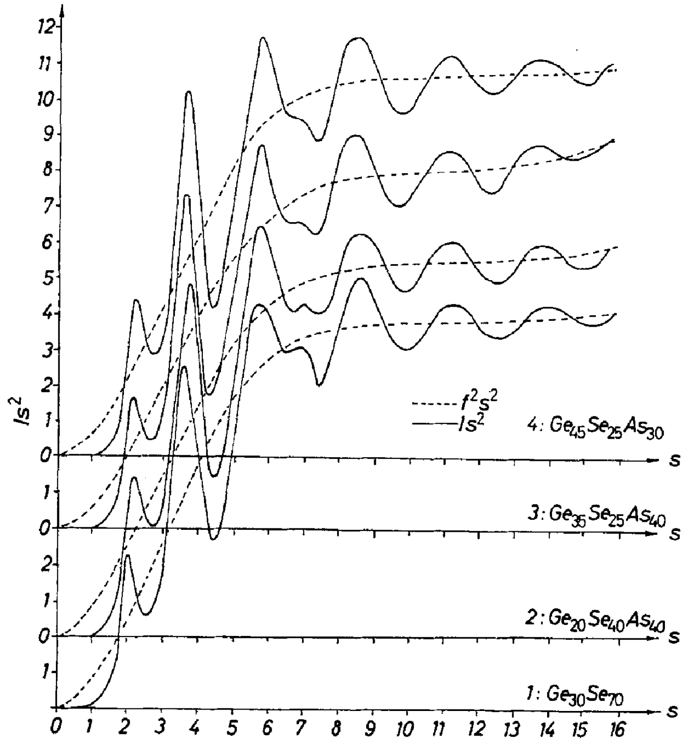

Fig. 3. Normalization curves. Corrected intensities times s^2 vs s; $\left(s = 4\pi \frac{\sin \theta}{\lambda}\right)$.

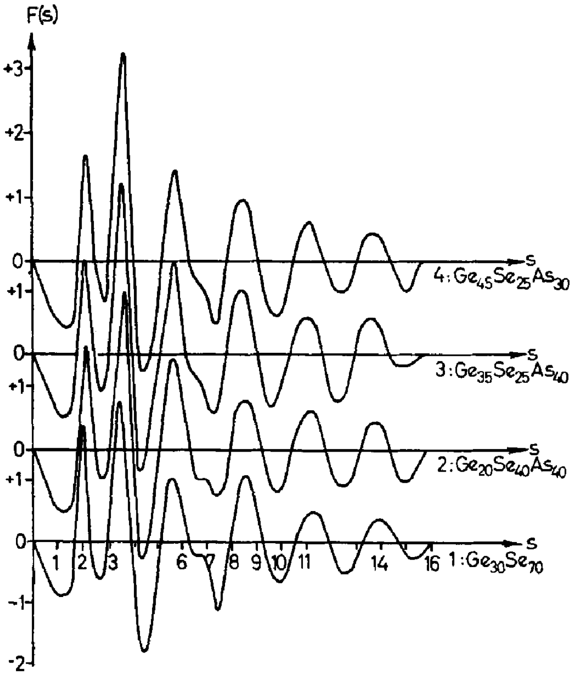

Fig. 4. $F(s)$ curves vs s.

order of the atoms in the glassy state. We have found a similarly high degree of order only in red phosphorus (*9*).

The so-called series termination effect was eliminated graphically by the method indicated in (*9*) and (*10*). Figure 5 shows the atomic distribution curves. The dashed curves were obtained without elimination of the series termination effect and the fully drawn curves by taking into account the series termination effect. The small negative values before the first maximum could not be eliminated. In order to eliminate these it would have been necessary to measure with AgKα-X-rays; but a 2 kW-Ag-tube was not at our disposal.

We must now interpret the atomic distribution curves obtained. This is difficult to do because it is generally not possible to conclude with certainty from a one-dimensional distribution curve to a three-dimensional arrangement. It is necessary to dispose a structure model whose statistics of atomic distances is then compared with the measured atomic distribution curve.

Within the precision of measurement, the positions of the first maxima correspond to the

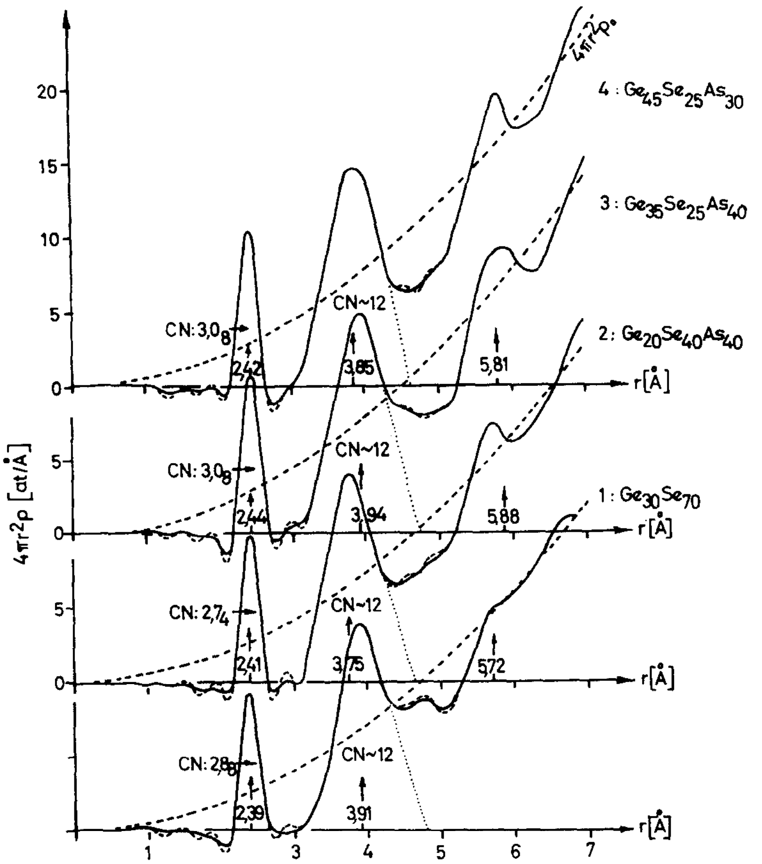

FIG. 5. Atomic distribution curves:

--- with series termination effects;

—— without series termination effects.

average of the calculatable covalent atomic distances (Table I)

The atomic distances and the bond angles in the glassy forms of As and Se (*11*) as well as in crystalline Ge are given in Table II.

These values were used for calculating the atomic distances which are to be expected theoretically in the glasses. One can see, that within the precision of measurement the values are in good agreement. The coordination numbers obtained also correspond to

TABLE I

CALCULATED AND OBSERVED ATOMIC DISTANCES AND COORDINATION NUMBERS IN THE GLASSES OF THE SYSTEM Ge–As–Se

Sample	Composition	r_1[Å] exp	r_1[Å] calc	r_2[Å] exp	Bond Angle	Coordination number exp	calc
1	$Ge_{30}Se_{70}$	2.39	2.39	3.9	109.4°	2.6_6	2.60
2	$Ge_{20}Se_{40}As_{40}$	2.41	2.43	3.75	103°	2.7_4	2.80
3	$Ge_{35}Se_{25}As_{40}$	2.44	2.44	3.94	107.8°	3.0_8	3.10
4	$Ge_{45}Se_{25}As_{30}$	2.42	2.44	3.85	104.6°	3.0_8	3.20

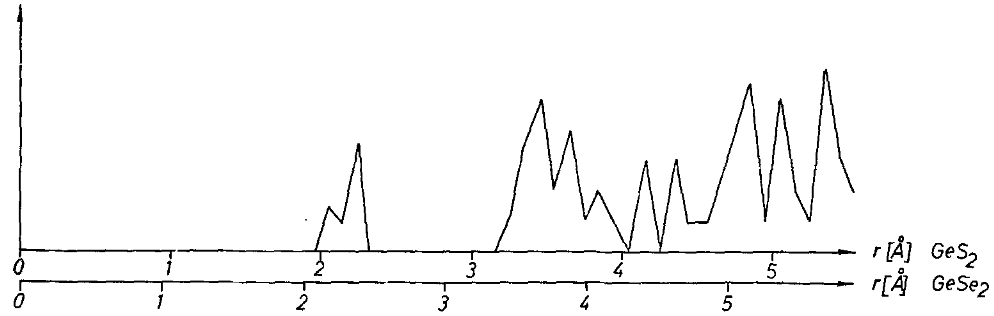

FIG. 6. Atomic distances in the GeS_2 structure and the calculated distances for an isostructural $GeSe_2$.

TABLE II

ATOMIC DISTANCES AND BOND ANGLES IN GLASSY Se AND As AND IN CRYSTALLINE Ge

	r_1[Å]	r_2[Å]	Bond Angle	Atomic Radii Å
$\mathrm{Se_{glass.}}$	2.36	3.72	104°	1.18
$\mathrm{As_{glass.}}$	2.49	3.78	98.75°	1.24_5
$\mathrm{Ge_{cryst.}}$	2.45	4.00	109.5°	1.22_5

the mean value of the calculated coordination numbers if one assumes for Ge the coordination number 4, for As 3, and for Se 2. The average bond angle can be calculated from the position of the second coordination maximum. The calculated bond angles are shown in Table I. The calculation of the bond angles is not exact because the distances of the next nearest atoms are close to the van der Waal distance and the two corresponding maxima more or less fall together in the atomic distribution curve.

At higher temperatures in the melt, the samples at the border of the glass forming area (*3*, *4*) already have a relatively high although not metallic conductivity (*7*). It was, therefore, possible to find atoms with distorted octahedral environment in the atomic distribution curves, i.e., a certain accumulation of atoms about a distance somewhat above 3.0 Å. We actually found a little difference to the atomic distribution curves of the samples 1 and 2 in this area. If this increase was real, this would mean that to a small extent atoms having distorted octahedral environment exist in the glass. No evidence was found for the assumption that the Ge has two neighbours in this case (*2*). On the contrary, Ge is surrounded by four atoms, As pyramidally by three atoms and Se has two neighbours in an angular arrangement.

Sample 1, whose composition corresponds approximately to the compound GeS_2, has the greatest bond angle corresponding to a tetrahedral angle. If one assumes that the atomic arrangement is similar to that of GeS_2, than one can consider the mean bond angle of this lattice for comparison. In GeS_2 the bond angle is the tetrahedron angle (i.e., 109.5°) for Ge and 103° for the bridging *S* atom, thus giving a mean angle of 106.5°.

Figure 6 shows the statistics of atomic distances for the GeS_2 lattice. In a GeS_2 lattice of corresponding structure one would have to assume 6% larger distances as the sum of the bond radii of S ($r = 1.025$ Å) and Ge ($r = 1.225$ Å) is 2.250 Å, whereas the sum of the bond radii of Se ($r = 1.17$ Å) and Ge is 2.395 Å. On the abscissa of Fig. 6, two scales are given which correspond respectively to the atomic distance statistics of GeS_2 and of $GeSe_2$, the scale being reduced by 6% for the latter. Therefore, it is probable that the short range order in the glass $Ge_{30}Se_{70}$ is similar to that of crystalline GeS_2.

The slight differences in the bond angles of the samples 2, 3, and 4 could not be interpreted. One should expect that a higher content of As would lead to a smaller valence angle but this was not found.

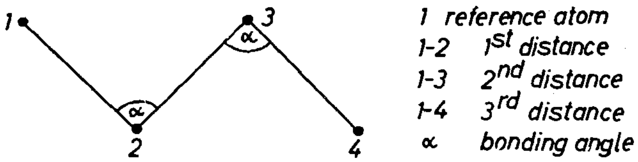

FIG. 7. Atomic arrangement in a plane for the calculation of the second and third distance.

TABLE III

COMPARISON OF EXPERIMENTAL AND CALCULATED ATOMIC DISTANCES OF THE THIRD NEIGHBOUR

Sample No.	r_3-exp [Å]	r_3-calc [Å]
2	5.72	5.83
3	5.88	6.05
4	5.81	5.94

Contrary to sample 1, the three samples show a third pronounced maximum at 5.7–5.9 Å. If one assumes that a series of four atoms are arranged in a zigzag manner in a plane independently of their further incorporation into the network (see Fig. 7) and if one uses the atomic distances and the bond angles obtained from the first two maxima, we find that the position of the third maximum agreed relatively well with the calculated values for the distance between the first and the fourth atom (see Table III).

Acknowledgments

The authors thank Mr. H. U. Gruber and Mr. H. Thurn for their assistance in performing the experiments and the calculations.

Financial support by the Deutsche Forschungsgemeinschaft, Bad Godesberg, and the Verband der Chemischen Industrie, Düsseldorf, is gratefully acknowledged.

References

1. A. A. VAIPOLIN AND M. A. PORAI-KOSHITS, *Proc. All Union Conf. Glassy State III Leningrad* 423 (1959).
2. A. R. HILTON, C. E. JONES, R. D. DOBROTT, H. M. KLEIN, A. M. BRYANT, AND T. D. GEORGE, *Phys. Chem. Glasses* **7**, 105 (1966).
3. J. A. SAVAGE AND S. NIELSON, *Infrared Phys.* **5**, 195 (1965).
4. S. V. NEMILOV, *Zh. Prikl. Khim.* **37**, 1452, 1699 (1965).
5. J. A. SAVAGE AND S. NIELSON, *Phys. Chem. Glasses* **5**, 82 (1964).
6. J. A. SAVAGE AND S. NIELSON, *Phys. Chem. Glasses* **6**, 90 (1965).
7. R. W. HAISTY, Thesis, Stuttgart, 1968; R. W. HAISTY AND H. KREBS, *J. Non-Cryst. Sol.* **1**, 427 (1969).
8. H. U. GRUBER AND H. KREBS, *Z. Anorg. Allg. Chem.* **369**, 184 (1969).
9. H. KREBS AND H. U. GRUBER, *Z. Naturforsch.* **22A**, 96 (1967).
10. R. HOSEMANN, K. LEMM, AND H. KREBS, *Z. Phys. Chem.* **41**, 314 (1964).
11. H. KREBS AND R. STEFFEN, *Z. Anorg. Allg. Chem.* **327**, 224 (1964).