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REACTIONS AND DIFFUSION IN THE SILVER-ARSENIC CHALCOGENIDE GLASS SYSTEM

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(Ph. D. thesis)

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REACTIONS AND DIFFUSION IN THE SILVER-ARSENIC CHALCOGENIDE GLASS SYSTEM

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ABSTRACT

The diffusion of Ag in amorphous As_2S_3 and As_2Se_3 at 175°C is accompanied with the reduction of As from a valence of +3 to +2 and +2 to +1 to maintain charge neutrality in the glass. The reactions for the sulfide and selenide glasses are identical. Ag^+ alone diffuses at this temperature, all other ions are essentially immobile. An amorphous reaction product phase is formed in the diffusion zone with a composition range of 28.6 to 44.4 atomic percent Ag. The lower limit corresponds to all As cations of +2 valence (amorphous $Ag_2As_2S_3$). The upper limit, the maximum solubility of Ag in these glasses, corresponds to all As cations of +1 valence (amorphous $Ag_4As_2S_3$). The diffusivity of Ag in these glasses at 175°C in the concentration range of 10 to 35 atomic percent Ag is

$$\text{Sulfide} - 4 \times 10^{-14} \exp(+0.23 \pm .01)(\text{atomic \% Ag})$$

$$\text{Selenide} - 2 \times 10^{-12} \exp(+0.14 \pm .01)(\text{atomic \% Ag})$$

I. INTRODUCTION

Diffusion is a consequence of thermodynamic nonequilibrium in a system. Measurable mass transport in glass at temperatures below the glass transition temperature (T_g) is only by cation movements. The anion structure is immobile; it is the basic nonyielding skeleton of the glass. Significant diffusion below T_g then becomes possible only if cation-cation or cation-electrical defect movement maintains electroneutrality.

Amorphous As_2S_3 and As_2Se_3 are "isomorphic" glasses. A two dimensional layer structure of short range order is formed where each As atom is bonded to three chalcogenide atoms in a flat triangular-pyramid arrangement; three chalcogenide atoms form the base and one As atom forms the apex. Each chalcogenide atom shares two pyramid bases thus fulfilling all of the covalent bonding requirements of cations and anions and extending the structure throughout three dimensional space. Ag diffusion in the sulfide and selenide glasses is expected to exhibit similar character.

Electrical properties of amorphous semiconductors have been extensively studied. Excellent reviews have been written by Adler,[1] Mott[2] and Thornburg.[3] The chemistry of these glasses, and of As_2S_3 and As_2Se_3 in particular, has not received the same degree of attention. Interfacial redox reactions in the Ag-As_2S_3 systems have been identified in the work of Matsuda and Kikuchi.[4] They report data on the thermal doping (170°C) and photodoping of thin films of the glass with Ag. Although not explicitly remarked on in the paper, their observation of crystalline As_2S_2 and Ag_2S peaks in the electron microprobe x-ray diffraction data constitutes the first report of interfacial redox reactions in the Ag—As chalcogenide

system. Reactions have been noted in Ag photodoping work but not specifically identified as redox reactions.[4,5,6,7]

Diffusion studies of Ag in amorphous As_2Se_3 were conducted by Stuptitz and Willert.[8] Radioactive (Ag^{110}) tracer experiments were performed in which a thin film (an area of 0.3 cm^2 covered by 10^{14} to 10^{16} atoms) of Ag was vacuum-evaporated on the glass. A diffusivity of 3 exp (-0.89 eV/kT) was determined. No concentration dependence and no interfacial reactions were reported. In a later work Lebedev, Stuptitz and Willert[9] reported the charge on the diffusing Ag (ion) to be (1.2 ± 0.2)e and the solubility to be 3 x 10^{-19} atoms/cm^3 (approximately 0.01 atomic percent). In the sulfide glass (As_2S_3) Goldschmidt and Rudman[5] reported up to 39 atomic percent of dissolved silver and DeNeufville[10] observed 30 atomic percent.

Goldschmidt and Rudman[5] studied the kinetics of the photodissolution of Ag in As_2S_3 glass. A thin film (300 Å) of Ag was deposited on a film (5000 to 25000 Å) of As_2S_3. Upon illumination of the interface through the glass film, the Ag dissolved (photodissolved) into the glass at room temperature. No interfacial redox reactions were specifically identified. It is noted here that diffusion typically becomes appreciable at half the absolute melting temperature of a glass solvent. As_2S_3 and As_2Se_3 glasses melt at approximately 300°C (573°K); half of this temperature is about room temperature (13°C). The kinetics of photodissolution include an illuminated induction time before dissolution commences. It was stressed that "radiation damage" during the initial induction period is essential for subsequent photodissolution.

Andreichin's[11,12] work on photopolarization illuminates the nature of Goldschmidt and Rudman's "radiation damage." When As_2S_3 glass was polarized with a constant electric field and illuminated, a transient current was observed indicating further polarization. The charge accumulated under the influence of light does not disappear immediately upon light extinction but decays with time (minutes to hours) in ambient light. With extinction of both electric field and all light, a metastable residual polarization remains (photoelectret polarization). Andreichin reports, "Since the conduction is purely electronic, we have neither dipoles, which would be orientated by the field, nor ions, which would move, nor any other similar species." He concludes, "The polarization phenomena in high resistance vitreous semiconductors are of a purely electronic, and not ionic, character."[12]

It is possible to explain photodissolution and photopolarization in terms of redox reactions involving electron transfer between cations. The core of this present work is the recognition of arsenic cation valence changes necessary for redox reactions that occur. However, application of this mechanism to explain other phenomena must be made with great caution. Ionic valence change in an amorphous semiconductor induced by illumination has not been documented; the photoreactions of arsenic chalcogenide glasses are dramatic,[6] intriguing[7] and not fully understood. Ionic valence change in an amorphous semiconductor induced by an applied electric field was first proposed by Drake, Scanlan and Engel.[13,14] This mechanism was used to explain the conductivity transition characteristic of these semiconductors. Copper-doped phophate glasses were investigated but the applicability of this model to arsenic chalcogenide glasses was specifically mentioned.[14]

Faure, Mitchell and Bartlett[15] report dissociative vaporization of As_2S_3 to the AsS and S_2 vapor species. Goldschmidt and Rudman[5] acknowledge this dissociation but only at high vaporization rates. They contend that at their low vaporization rates As_4S_6 is the predominate vapor species. Their films deposited in this manner were reported to be As_2S_3.

Various valences of arsenic in a selenium anion environment have been reported. Dembrowki[16] conducted a careful analysis of the As-Se binary system. Thermographic records of the preparation of the alloys from the elements throughout the entire concentration range were obtained. Exothermic maxima indicated the formation of the compounds As_2Se_5, As_2Se_3, AsSe and As_2Se; the arsenic valences are, respectively, +5, +3, +2 and +1.

The objectives of the present study are to determine the reactions and diffusion of Ag in bulk arsenic chalcogenide glass below the transition temperature of the glass. These data also provide solubility information. Glass modifier diffusion in glass is typically concentration dependent. One of the objectives is to determine the concentration dependence of Ag diffusion in these glasses.

II. EXPERIMENTAL PROCEDURES

Glass Fabrication

Amorphous arsenic (99.9999%),* selenium (99.999%),** and arsenic sesquisulfide (99%),*** weighed to the appropriate amount, were encapsulated in evacuated fused silica ampules. These were heated to 600°C at 6°C/

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*Gallard Schlesinger Chemical Mfg. Corp., Carle Place, NY.

**Orion Chemical Co., Glendale, CA.

***Pfaltz and Bauer Inc., Flushing, NY.

minute while rocking in a furnace (one rock/minute) and held rocking for 48 hours, then water quenched. Rocking the ampule insured glass homogeneity. The rocking frequency and glass viscosity at 600°C were in accord to allow the glass to flow to either side of the ampule each minute providing thorough mixing.

Couple Fabrication

Glass-silver salt planar diffusion couples were fabricated by first polishing the components down to 0.3 micron. Couples were then held together with alligator clips during heat treatment and subsequent potting. These clips allowed perfect alignment. The clip end extending out of the epoxy potted sample was amputated, and the sample was polished exactly perpendicular to the planar interface. The interface was so fragile that this "sacrificial alligator clip" technique was necessary to preserve the integral couple through the heating and potting procedure. Extra care was taken during polishing since the heat treated glass was very brittle.

Oxidation

The time vs. distance diffusion data for selenide couples exhibited anomalous scatter. It is believed that an oxide film (As_2O_3, SeO_2) on the surfaces prevented interface formation until the film was dissipated at 175°C by evaporation and/or solution in the glass. Assuming that ΔH_f^o of As_2Se_3 is within 20 kilocalories of the ΔH_f^o of As_2S_3, the reaction and enthalpy change[17,18] are given by

$$\begin{array}{lcccc} & As_2Se_3\ (s) + 9/2\ O_2\ (g) & = & As_2O_3\ (s) + 3\ SeO_2\ (s) & \\ \Delta H_f^o \text{ values} & -33 \pm 20 & & -157 \qquad 3(-55)\ \text{kcal} & \end{array} \tag{1}$$

ΔH^o for the reaction then is -289 ± 20 kcal. The standard entropy for this reaction is primarily a consequence of condensation of 9/2 moles of oxygen gas. This is approximately 44 entropy units per mole, and at 273°K contributes approximately 54 kilocalories to the standard free energy of reaction so that the resultant free energy change for this reaction is of the order of -235 kilocalories.

Oxygen was identified by electron emission data as a surface contaminent. Electron spectroscopy chemical analysis (ESCA) techniques were used to determine the chemical environment of As and Se in As_2Se_3 glasses with varying amounts of Ag. To form bulk homogeneous specimens, As_2Se_3 and powdered silver metal were crushed and mixed in air with a mortar and pestle. This mixture was pressed into a pellet and heated in argon at 175°C for 48 hours. Crushing the glass in ambient air introduced oxide contamination. Subsequent heat treatment put some of the surface As and Se oxides into solid solution in the selenide glass. ESCA results clearly identified oxygen as a major bulk constituent. Data for a virgin piece of bulk As_2Se_3 glass, free of oxygen, matched that in the literature, indicating proper ESCA technique.[19] Time limitations prevented further experiments.

These experiments did reveal, however, that argon sputter cleaning of the glass surface in the ESCA vacuum chamber created an excellent electrically conductive surface on all samples. Typical surface charging problems indigeneous to insulators were not encountered.

Explosion

Powdered Ag_2S was sealed in an evacuated fused silica ampule and heated in order to form a dense solid by melting and quenching. At about

550°C (mp = 842°C) the ampule exploded. This phenomenon was repeatable. Apparently oxygen, in the form of Ag_2O, was sorbed on the starting sulphide powder allowing the following exothermic reaction to take place:

$$2\ Ag_2O\ (s) + Ag_2S\ (s) = 6\ Ag\ (s) + SO_2\ (g) \qquad (2)$$

At 700°K, the ΔH^o for this reaction is -59 kilocalories.[17,18] The entropy change is favorable.

To form polycrystalline $AgAsS_2$ (smithite) from As_2S_3 and Ag_2S, without explosion, the mixture was heated in an evacuated fused silica ampule according to the time-temperature schedule indicated in Fig. 1. Formation of smithite was identified by x-ray analysis. $AgAsS_2$ melts at 417°C and at the test temperature of 175° it is stable in contact with As_2S_3 (Fig. 2).[20]

Silver Plating

Glass-metal diffusion couples were fabricated by plating silver (Fig. 3) on polished glass specimens. Surface conduction varied; surfaces covered with oxide films had the lowest conduction. Oxide covered glasses had the silver plating initiate at the point of contact of the electrical connector (alligator clip with as-received cadmium plated or silver plated surface) with the glass surface. The silver film grows laterally in dendrites from the point of contact across the face of the polished glass (millimeters/minute velocity). Further lateral growth continues until the glass specimen is totally encapsulated.

To reduce the oxide growth, typical polishing techniques were conducted with modification of the final step. Glass specimens were lapped in a slurry of heptane or alcohol and 0.3 micron alumina. Thereafter, they were immersed in heptane or alcohol until plated. Before

immersion in the plating bath the glass specimen was connected to the negative 1 1/2 volt potential. This procedure was empirically observed to retard oxide growth. With this preparation the silver plate initiated smoothly, although sometimes spottily, over the glass surface after an incubation time of one or two minutes.

The most satisfactory method was to first form a drop of As_2Se_3 glass and then quench it on the wall of an evacuated fused silica ampule. When it was removed and immediately plated, the drop had sufficient surface conductivity to form a silver film evenly across the entire surface seconds after immersion in the plating bath. The surface of the quenched liquid drop is expected to consist of selenium anions arranged to best screen the arsenic cations. After heat treatment, this plated drop exhibited (Fig. 4 - Sample 46) an even thickness of reaction product phase. Polished, plated and heat treated specimens typically revealed an uneven thickness of reaction product phase.

Diffusion Analysis

All diffusion runs were conducted at 175°C. T_g of As_2S_3 and As_2Se_3 is 205° and 180°C, respectively.[1,3] The furnace was evacuated to less than 5×10^{-6} torr and backfilled with argon to minimize oxygen contamination. Temperature was monitored with a copper-constantan thermocouple to ± 2°. Extreme care was exercised in heating the furnace to 175°C to avoid overshooting this temperature and exceeding the T_g of the glass.

The silver, arsenic, and chalcogenide profiles of the diffusion couples were determined using an electron microprobe analyzer.* The

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*Model 400, Materials Analysis Co., Palo Alto, CA.

electron microprobe is a combination of a conventional x-ray tube (where the sample is the target), a tunable x-ray emission spectrograph (where the analyzing crystals are the diffraction monochrometers), a light microscope and a scanning electron microscope. All are enclosed in a common vacuum chamber. The sample to be analyzed is bombarded by a beam of monoenergetic electrons to excite the characteristic x-radiation of the elements in the specimen. The primary x-ray intensities emitted from the sample and a standard are then compared to obtain quantitative data on the concentration of each element in the sample. Corrections for absorption, fluorescence, atomic number, dead time, drift, and background are made to improve the accuracy of the analysis.[21,22]

The concentration profiles were obtained by traversing the electron beam along a desired path perpendicular to the diffusion couple interface which is perpendicular to the polished surface. An interegrated count per 40 seconds at a location was monitored by logic circuit counters and simultaneously punched on IBM cards for the introduction of corrections by computer. The beam was then advanced by a fixed distance (2 microns minimum) and the procedure was repeated.

Excessive heating, which caused evaporation or melting of the glass and/or surface diffusion of the silver, was eliminated by rapidly scanning the electron beam parallel to the interface of the couple during the counting at each point. This procedure reduced the incident energy per square micron per second on the couple. The minimum scan width for damage free operation was 80 microns. This technique yields an average composition over the 80 micron width; hence, planar geometry is essential. Moreover, extrapolation of the plotted profile is sometimes necessary to compensate

for irregular interfaces. The standards were also analyzed by the same scanning method; inaccuracies introduced by the decreased x-ray intensity as the beam deviates from the perfect focal point were thereby nearly eliminated.

Surface diffusion of silver activated by the incident electron beam was minimized by stepping the scanning beam a minimum step length of two microns and always proceeding from silver-lean to silver-rich areas. Characteristic x-ray counts during the 40 second counting time were just sufficient to give well-defined statistics for good but not excellent data. A maximum of three elements can be simultaneously detected; a fourth can be quantitatively determined by difference via computer compilation. Three element data were accurate to ± 2 atomic percent. In this work diffusion couples contained three elements.

For qualitative chemical analysis an EDAX analyzer* (Energy Dispertion Analysis of X-rays) was used. This instrument is a modified microprobe analyzer where the entire spectrum of emitted x-rays is analyzed.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The core of the experimental results is the diffusion profiles of the Ag metal-As_2S_3 glass (Fig. 5), Ag metal-As_2Se_3 glass (Figs. 6 to 8) and polycrystalline Ag_2Se-As_2Se_3 glass (Figs. 9 to 12) diffusion couples. The temperature was 175°C for all of the runs; the time is noted in each

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*Model 711, EDAX Inc., Prairieview, IL.

figure. The interpretation and analysis of these profiles can yield chemical reaction, solubility and diffusion data for these systems. The profiles reveal that redox reactions occur. The formation of an amorphous reaction product phase is observed and the composition limits are determined. A Boltzmann-Matano analysis is applied to determine diffusivity data.

Ag Metal-Glass System

(a) Diffusion Profiles

A large number of Ag-glass couples were fabricated. Initially, extreme difficulties were encountered in microprobe analysis procedures before repeatable data were generated. Several runs were selected on the basis of the required Boltzmann-Matano criteria and shown in Figs. 5 to 8. Table 1 lists critical profile data. The experimental error in these measurements is ± 2 atomic percent.

The number of cations per 100 anions vs. distance are plotted in the figures above each profile on the same distance axis. The As content remains constant at 66 throughout the diffusion zone and into the bulk chalcogenide glass. This indicates the As cations, of any valence, are immobile in the immobile anion structure. The Ag cations alone are mobile at $T < T_g$. The gradient in concentration of As ions is a consequence of a percentage change due to the introduction of Ag ions into the glass and not to As movement.

(b) Reactions

The nature of the profiles indicates that redox reactions occur. A charge balance analysis of ion concentrations at any location in the diffusion zone shows that the As is reduced from a valence of +3 to +2

Table 1. Reaction Phase Composition Limits

Stoichiometric Compositions	As_2S_3	$Ag_2As_2S_3$	$Ag_4As_2S_3$
	all As^{+3}	all As^{+2}	all As^{+1}
		28.6 % Ag	44.4 % Ag
	60% S or Se	42.9 % S or Se	33.3 % S or Se
	40% As	28.6 % As	22.2 % As
		Glass-Metal Couples	
#42 Fig. 5		29 % Ag	42 % Ag
As_2S_3-Ag		42 % S	36 % S
175°C-120 hrs.		29 % As	23 % As
#46 run 1 Fig. 6		28 % Ag	44 % Ag
As_2Se_3-Ag		41 % Se	33 % Se
175°C-5 hrs.		28 % As	22 % As
#46 run 2 Fig. 7		30 % Ag	44 % Ag
As_2Se_3-Ag		40 % Se	34 % Se
175°C-5 hrs.		30 % As	22 % As
#45 Fig. 8		29 % Ag	41 % Ag
As_2Se_3-Ag		41 % Se	35 % Se
175°C-5 hrs.		29 % As	23 % As

and then from +2 to +1 in order to maintain charge neutrality in the glass with the introduction of Ag. Identical redox reactions appear to occur in the silver-arsenic sulfide and silver-arsenic selenide systems. The interpretation of the profile data, augmented with thermodynamic data, is the following.

Initially the Ag is oxidized at the glass interface by the glass:

$$2\ Ag + As_2S_3 = As_2S_2 + Ag_2S \qquad (3)$$

$$\Delta H^o = -6.25 \pm 6.1\ \text{kcal}$$

The As^{+3} is reduced to the +2 valence state. The resulting products form a glass with the composition of $Ag_2As_2S_3$ with the reduction of all As^{+3} to As^{+2}. At intermediate stages every Ag atom oxidized requires a reduction of one As^{+3} to As^{+2}, and the equation can be written as

$$x\ Ag + As_2S_3 = As^{+3}_{2-x}As^{+2}_{x}Ag^{+1}_{x}S_3 \qquad (4)$$

where x varies from 0 to 2. The diffusion of Ag^+ into the glass requires this reduction in order to maintain electrovalent balance. Experimental results indicate that further solution of Ag by the glass promotes further reduction of the arsenic:

$$Ag + As^{+2} = Ag^+ + As^+ \qquad (5)$$

The resulting equation for the intermediate stages when an As^{+2} is reduced to an As^{+1} by an entering Ag can be written as

$$x\ Ag + As_2Ag_2S_3 = As^{+2}_{2-x}As^{+1}_{x}Ag^{+1}_{2+x} \qquad (6)$$

where x varies from 0 to 2. The transition point for Eqs. 4 and 6 occurs at the intersection of the As and Ag concentration curves in the diffusion profiles. Reduction of arsenic to the elemental state, however, is not

favored thermodynamically:

$$As_2S_3 + 6\ Ag = 2\ As + 3\ Ag_2S \tag{7}$$

$$\Delta H^o = +\ 10.35 \pm 3.3\ \text{kcal}$$

$$As_2S_2 + 4\ Ag = 2\ As + 2\ Ag_2S \tag{8}$$

$$\Delta H^o = +16.6 \pm 3.2\ \text{kcal}$$

Thermodynamic data for the selenides are unavailable. However, the similar chemical nature of sulfur and selenium anions and the observed identical reaction product compositions justify the conclusion of identical redox reactions. In subsequent discussions sulfur and selenium are used interchangeably.

A strikingly similar cation valence change in crystal chemistry exists in the case of tungsten bronze.[23-25] For instance, sodium tungsten bronze has the ideal composition $NaWO_3$, with the perovskite structure, but this compound shows variable composition. It is better represented by the formula Na_xWO_3 with $1 > x > 0$. To preserve neutrality one tungsten ion is converted from W^{+6} to W^{+5} for every sodium ion accomodated.

(c) The Reaction Product Phase

An amorphous reaction product phase is observed to form. Considering the redox reactions developed in the preceeding section, it is observed that secondary phase formation occurs when the Ag content is sufficient to reduce all As^{+3} in the original As_2S_3 to As^{+2} and As^{+1}. By definition a phase is any portion of a system which is physically homogeneous within itself and bounded by a surface so that it is mechanically separable from any other portions.[26] Sharp boundaries are observed (Fig. 4) at the cross over points for the As and Ag profiles. This appearance of the reaction

product phase is enhanced by etching under ultrasonic vibration 15 to 30 seconds in 1N KCN solution. Electron microprobe profiles show smooth and continuous Ag gradients across the boundary indicating the existence of complete solid solution between the two phases. The portion containing As^{+3} corresponds to the solution of Ag in the original As_2S_3 glass phase.

As indicated in Table 1, if all the arsenic is reduced to the +1 valence, the stoichiometry of the amorphous reaction product phase would be:

$Ag_4As_2S_3$ = 44.4 atomic % Ag
33.3 atomic % S or Se
22.2 atomic % As

If all the arsenic is reduced to the +2 valence, the stoichiometry of the amorphous solid solution reaction product phase would be:

$Ag_2As_2S_3$ = 28.6 atomic % Ag
42.9 atomic % S or Se
28.6 atomic % As

The transition point then would correspond to a composition of 29 atomic percent As and Ag. Within experimental error, the composition at the interface or crossover point was found to equal this value (Table 1). It is also evident from the viewpoint of solubility that 44.4 atomic percent is the maximum theoretical solubility limit of Ag^+ in As_2S_3 glass. This value is in excellent agreement with the experimental data.

(d) Oxidation

Interfacial oxide contamination in these couples, as discussed earlier, is believed to be responsible for variations in the interfacial Ag concentration and the thickness of the diffusion zone because of the

resulting difficulties in forming a true interface. Figure 8 (sample 45) exhibits an anomolously short Ag profile (40 microns) compared with Fig. 6 (125 microns, sample 46 run 1) and Fig. 7 (140 microns, sample 46 run 2). Both samples were held for 5 hours at temperature.

Sample 46 was polished as described to reduce oxygen contamination. Sample 45, on the other hand, had a final glass polishing step in an aqueous slurry and was stored several days before plating resulting in surface oxidation. The samples also showed different surface conductivities during Ag plating. It is thus postulated that a large portion of the heat treatment was utilized by sample 45 to dissolve the oxide layer before a true interface formed and diffusion began. Possible oxide vaporization was prevented as the glass was encapsulated by the silver metal.

<u>Ag_2Se-As_2Se_3 Glass System</u>

Ag_2Se-As_2Se_3 couples exhibit diffusion profiles similar to the Ag metal-As_2Se_3 glass profiles. Figure 9 through 12 are profiles representative of this system and Table 2 lists critical profile data. The similarity of diffusion profiles indicates that a reduction of As^{+3} also occurs in this system which can be accomplished only by the availability of Ag. Ag becomes available from Ag_2Se by the oxidation of Se^{-2} ions to elemental Se. This reaction is unique in that it was expected that interdiffusion between Ag and As would occur with the possible formation of $AgAsSe_2$ which would be analagous to $AgAsS_2$, smithite.

(a) Reactions

In this system a reaction product phase is formed similar to the Ag metal-glass system. Ag is dissolved in the glass with a reduction of As^{+3} to As^{+2} or As^{+1} as indicated by the constancy of the As/Se ratio in

Table 2. Reaction Phase Composition Limits

Stoichiometric Compositions	$Ag_2As_2S_3$	$Ag_4As_2S_3$
	all As^{+2}	all As^{+1}
	28.6 % Ag	44.4 % Ag
	42.9 % Se or S	33.3 % Se or S
	28.6 % As	22.2 % As
	Glass-Silver Salt Couples	
#25 Fig. 9	28 % Ag	40 % Ag
As_2Se_3-Ag_2Se	43 % Se	35 % Se
175°C-21.6 hrs.	28 % As	24 % As
#27 Fig. 10	30 % Ag	
As_2Se_3-Ag_2Se	40 % Se	
175°C-30.8 hrs.	30 % As	
#31 Fig. 11	28 % Ag	46 % Ag
As_2Se_3-Ag_2Se	43 % Se	31 % Se
175°C-25 hrs.	28 % As	22 % As
#40 Fig. 12	28 % Ag	42 % Ag
As_2Se_3-Ag_2Se	41 % Se	30 % Se
175°C-12.3 hrs.	28 % Se	26 % Se

the diffusion zone and extending into As_2Se_3 (Figs. 9 to 12). The following equations, which are similar to Eqs. 4 and 6, represent the reactions:

$$As_2Se_3\ (gl) + Ag_2Se\ (xtal) = Ag_2As_2Se_3\ (gl) + 1/2\ Se_2\ (g) \qquad (9)$$

$$Ag_2As_2Se_3\ (gl) + Ag_2Se\ (xtal) = Ag_4As_2Se_3\ (gl) + 1/2\ Se_2\ (g) \qquad (10)$$

An accumulation of Se was not observed at the interfaces; it thus left the interfaces as a vapor. These endothermic reactions have an entropy contribution due to the vapor species in the reaction product. Therefore, they are thermodynamically favorable at elevated temperatures.

An experiment was devised to prove the existence and analyze the composition of the vapor reaction product. An As_2Se_3-Ag_2Se couple was sealed in a 45 cm. long pyrex tube filled with 0.9 atmosphere of argon. Every precaution had been taken to prevent oxidation of the chalcogenide glass surface. The end of the tube with the couple was held at 175°C for 48 hours. The other end extended out of the furnace allowing it to be at room temperature. A condensate of many small islands of relatively pure selenium formed in the cool end of the tube as seen in Fig. 13. These were identified by EDAX. Selenium was also identified on the cadmium plated alligator clip that held the diffusion couple together. Pyramids, containing mostly arsenic and some silicon, were also found; oxygen may also have been present but could not be detected by this analyzer. These pyramids are considered to be extraneous to the reaction of concern. Their presence could be explained as follows: At 175° some vaporization of As_2Se_3 occurred in 48 hours. Vaporization may be dissociative similar to the sulfide with AsSe and Se_2 as the gaseous species. The arsenic selenide species was reduced to the elemental form by the cadmium plated

clip. This As vapor was transported and then condensed and reacted with the glass to form the pyramids. A quantitative mass balance was not possible because of the nature of the experiment. However, the total amount of selenium on the cadmium plated clip and the glass tube appeared to be far in excess of 3/2 of the arsenic in the pyramids on the glass. Therefore, the source of selenium would have to include the Ag_2Se oxidation reaction, and Eqs. 9 and 10 are validated. The kinetics of these reactions are controlled by the rate of escape of the chalcogenide vapor and not the time allowed for reaction.

(b) Diffusion Profiles

The couple of Fig. 10 shows a reaction rate limited process since the maximum solubility of Ag in the glass and the formation of the reaction product was not realized after 30.8 hours at 175°C. The couple of Fig. 11 shows the formation of the reaction product and a diffusion limited process even though it was held at 175° for the shorter time of 25 hours. It is thus postulated that the Se was able to escape more readily in the later case. Consideration of the geometry of the couples justifies the conclusion that the kinetics are controlled by the rate of escape of the vapor reaction product.

Planar diffusion couples always opened like a clam shell, pivoting about a small volume of material where the interface was formed. The extent of "clam shell" opening and hence, the ability of the vapor to escape, varied randomly. Accordingly, the extent of the rate at which Ag was supplied to the glass phase varied randomly. Oxygen contamination undoubtedly also contributes to the variability of the results as discussed before.

It is expected that a diffusion couple formed so that Se could not escape would show essentially no compound formation. The reaction would require chemical interdiffusion of 3 Ag^{+} and As^{+3} which is energetically difficult at 175°C. $AgAsS_2$ (smithite) was formed by mixing Ag_2S and As_2S_3 in the liquid state in a closed container. When a diffusion couple of polycrystalline $AgAsS_2$ and As_2S_3 glass was formed, no Ag diffusion was observed after 400 hours at 175°C. This result is in conformity with the Ag_2S-As_2S_3 phase diagram (Fig. 2) which shows that $AgAsS_2$ is in equilibrium with As_2S_3 at 175°C. It also indicates that the solid solution of one component in the other is very low and below the detectable limit since the test temperature of 175°C is above half of the absolute melting point of $AgAsS_2$ (690°K/2 = 72°C).

The couple of Fig. 12 is of interest since it was accidently heated above T_g when the furnace temperature was being adjusted to 175°C. This temperature was not specifically known, but it was less than 250° for less than 30 minutes. Above T_g, reaction of Ag_2Se with As_2Se_3 occurs with a subsequent change in the As/Se ratio. This change is an indication of the loss of rigidity of the glass structure which exists below T_g. This deviation was retained on dropping below T_g. Subsequent diffusion occurred by reduction of As^{+3} as in previous profiles.

Diffusion

The diffusion process is an electrochemical reaction generated diffusion represented by movement of Ag^{+} and a corresponding electron to provide reduction of As ions for the advancing reaction zone. The anions and all As cations are essentially immobile. The diffusion mechanism includes a progression of steady state environments of As^{+3}-As^{+2} or As^{+2}-As^{+1} concentrations in the glass. For any specific concentration of

Ag there is one unique combination of As^{+3}-As^{+2} or As^{+2}-As^{+1} allowed by electroneutrality for an invarient number of As and S or Se atoms. Therefore, the progression of these nonequilibrium states under a chemical potential gradient with increasing Ag concentration is identical for every couple reported in this study. This condition is dependent upon the mobility of Ag^+ and electrons in these compounds.

Movement of Ag^+ and electrons in the stable charge density of the As cations and chalcogenide anions can create a local electrical potential field. Cation diffusion is then opposed by the potential field. This field may be quickly eliminated if the mobilities of the diffusing species are sufficiently high in the field at the elevated diffusion temperature. The mobility of Ag^+ in glassy As_2Se_3 at 180°C under an electric field is 1×10^{-8} cm^2/volt sec.[9] Holes are identified[27] as the mobile species for electronic conduction in these glasses. The drift mobility of holes at fields of 10^5 volt/cm is approximately 3×10^{-5} cm^2/volt sec[1]. It is assumed that the mobility of holes is high enough to eliminate the potential field.

Glass modifier diffusion in glasses is typically concentration dependent. A Boltzmann-Matano analysis must then be applied which is valid if the following assumptions are justified:

1) the diffusion is isothermal, isotropic and one-dimensional
2) the diffusion is not reaction rate limited
3) there is no volume change with introduction of the diffusing species
4) the driving force for diffusion is a gradient in the chemical potential of the diffusing species (negligible electrical

potential field)

Experimental procedure validates assumption #1. Assumption #2 is valid on the basis of constant compositions at the metal interface for a given temperature and on the basis of the expected interface compositions from the reaction calculations. The third assumption of no volume change is questionable. These glasses have an open structure that presumably can accomodate glass modifiers without extensive expansion although the amount of dissolved Ag is large. It was not possible to make expansion measurements because of the small volume of the diffusion zone. The fourth assumption has been discussed.

The bases for all diffusion theory are Fick's first and second laws, which are

$$J_i = -D \frac{\delta c_i}{\delta x} \tag{11}$$

$$\frac{\delta c_i}{\delta t} = D \frac{\delta^2 c_i}{\delta x^2} \tag{12}$$

where J_i is the flux of species i passing a plane of unit area per unit time, c_i is the concentration of species i per unit volume of material, t is time, and D is the diffusion coefficient or diffusivity which is not a function of concentration of i and has the units of cm^2/sec. If D is a function of concentration, Fick's second law is written as

$$\frac{\delta c}{\delta t} = \frac{\delta}{\delta x} \left(D \frac{\delta d}{\delta x} \right). \tag{13}$$

A solution for this general case is given by Boltzmann's approach[28] as

$$D_{c_i} = - \frac{1}{2t} \frac{dx}{dc} \int_0^{c_i} x \, dc, \tag{14}$$

provided that the following conditions are met:

(a) the process is diffusion-controlled, i.e., $x_{c_i} = kt^{1/2}$;

(b) $x = 0$ is defined by $\int_0^{c_o} x\, dc, = 0$;

(c) at $t = 0$, $c_i = 0$ for $x > 0$,

$c_i = c_0$ for $x < 0$.

The process is diffusion controlled if the Ag concentration at the Ag rich interface for these couples is found experimentally to be 44.4 atomic percent. The location of $x = 0$ is the Boltzmann-Matano interface (BMI). If there is no volume change with the introduction of interdiffusing species, this BMI is the location of equal and opposite diffusion fluxes. However, in each of these two systems there is only one component diffusing (Ag metal going into solution). The BMI, the original interface, is invariant; therefore, it is the Ag-glass interface revealed by the profile. It is assumed there is no volume change in this solution process. The dissolution of Ag from Ag_2Se is accompanied by the vaporization of Se. The original interface is again invarient.

The profiles of Figs. 5, 6, 7 and 11 were analyzed to determine Ag diffusivity data. On the basis of previous discussions these couple profiles are considered to be the most representative. Indications were that the diffusion was not reaction limited and that oxide contamination was at a minimum. The diffusivities calculated from Eq. 14 are shown in Fig. 14. The concentration dependence of diffusivity is apparent, the sulfide being more sensitive than the selenide. Inherent in this graphical analysis is an increasing inaccuracy as the extremities of the curves are approached. Diffusivity values below 8% and above 42% Ag were thus not plotted.

0 0 1 3 4 9 0 2 5 4 4

The concentration dependence of Ag diffusion into the As chalcogenides can be approximated as being exponential between the values of 10 and 35% Ag:

sulfide — $4 \times 10^{-14} \exp(+0.23 \pm .01)$(atomic % Ag)

selenide — $2 \times 10^{-11} \exp(+0.14 \pm .01)$(atomic % Ag)

The concentration dependence of Ag diffusion increases rapidly from 35 to 44% Ag. It should also be observed that the diffusivity varies smoothly across the reaction product phase composition limit of 29% Ag in either glass.

CONCLUSIONS

Silver diffusion in As_2S_3 and As_2Se_3 glasses (below T_g) is accompanied by reduction of the As cations from a valence of +3 to +2 or +2 to +1 to maintain charge neutrality. Reduction to the elemental state does not occur. In metal-glass couples oxidation of Ag provides electrons for As reduction. When Ag_2S or Ag_2Se salt is the source of silver ions for diffusion, some S or Se in the salt is oxidized to the elemental vapor state thereby providing the necessary electrons. In salt couples without arsenic reduction, chemical interdiffusion of cations is the only other possible diffusion mechanism. Cation interdiffusion does not occur readily.

An amorphous phase is formed when all As^{+3} is reduced to the +2 valence state. As^{+1} is miscible in this reaction product phase. The maximum solubility of Ag in As_2S_3 or As_2Se_3 is 44.4 atomic percent which occurs when all As is reduced to the +1 valence state. It was also found that As^{+2} is soluble in the original glass phase. The solution of Ag in these chalcogenide glasses thus can vary continuously from 0 to 44.4

atomic percent with an As valence change in appropriate proportion to maintain charge neutrality. Considering the amorphous reaction product phase, a new phase forms when the solubility exceeds 28.6% Ag.

The solubilities of Ag in As_2S_3 of 39 atomic percent by Goldschmidt and Rudman[5] and 30 atomic percent by DeNeufville[10] are dubious on two counts. First, their work was with vapor deposited thin films of "As_2S_3." The dissociative vaporization of As_2S_3 suggests that their thin films may contain ratios of As/S other than 2/3. Secondly, it has been shown that oxygen contamination of the chalcogenides occurs very readily and that its presence interferes with the formation of a true interface which is necessary for the indicated redox reactions to occur. It is postulated that their data is in error due to a combination of these problems.

For Ag diffusion below T_g of the glass, the As/S or As/Se ratio is invarient at 0.67 across the reaction product and into the bulk glass. This invarience indicates the anions and arsenic cations, of any valence, are immobile. Only Ag cations are mobile. The only similar metal-glass profiles in the literature are those of Matsuda and Kikuchi[4] for the Ag-As_2S_3 system. Their data were qualitative, the ordinate of the profiles (concentration) was not graduated. A self comparison of their data indicates that the As/S ratio varied in both thermally doped (170°C) and photodoped (room temperature) profiles. Sulfur depletions were apparent in portions of the glass film. It is believed that dissociative vaporization during the vapor deposition of the chalcogenide glass film caused the sulfur depletions.

Ag can be used for making an electrical contact to As chalcogenide containing amorphous semiconductors. It follows from these observations

that the optimum contact would be formed by consecutive deposition of the amorphous semiconductor film and the Ag contact film without breaking vacuum. This would eliminate oxide film formation. Pristine glass surfaces were found to have excellent surface conduction. The opposite is true for oxide covered surfaces.

From 10 to 35 atomic percent Ag concentration, the diffusivity at 175°C is

$$\text{sulfide} - 4 \times 10^{-14} \exp(+0.23 \pm .01)(\text{atomic \% Ag})$$

$$\text{selenide} - 2 \times 10^{-12} \exp(+0.14 \pm .01)(\text{atomic \% Ag}).$$

The concentration independent diffusivity of Ag in As_2Se_3 reported by Stuptitz and Willert[8] is 3×10^{-11} cm^2/sec at 175°C (Ag concentrations $\leq$ 0.01 atomic percent). Compared to the present results, this diffusivity value corresponds to diffusion in the original glass phase. Diffusivity values in this work were not obtained below 8 atomic percent Ag. Therefore, exact correlation with their results is not possible. Assuming that the diffusion activation energy of Stuptitz and Willert is concentration independent and combining it with the concentration dependence determined in this work, the diffusivity of Ag in As_2Se_3, in the concentration range of 10 to 35 atomic percent, at temperatures below T_g is

$$0.02 \exp \left[-0.89 \text{ eV/kT} + (0.14 \pm .01)(\text{atomic\% Ag})\right].$$

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FIGURES

1. Time-temperature schedule for $AgAsS_2$ formation.

2. Ag_2S-As_2S_3 binary phase diagram.

3. Silver plating assembly.

4. Microphotograph of sample 46.

5. Sample 42 profile: Ag-As_2S_3 couple, 120 hrs.

6. Sample 46 run 1 profile: Ag-As_2Se_3 couple, 5 hrs.

7. Sample 46 run 2 profile: Ag-As_2Se_3 couple, 5 hrs.

8. Sample 45 profile: Ag-As_2Se_3 couple, 5 hrs.

9. Sample 25 profile: Ag_2Se-As_2Se_3 couple, 21.6 hrs.

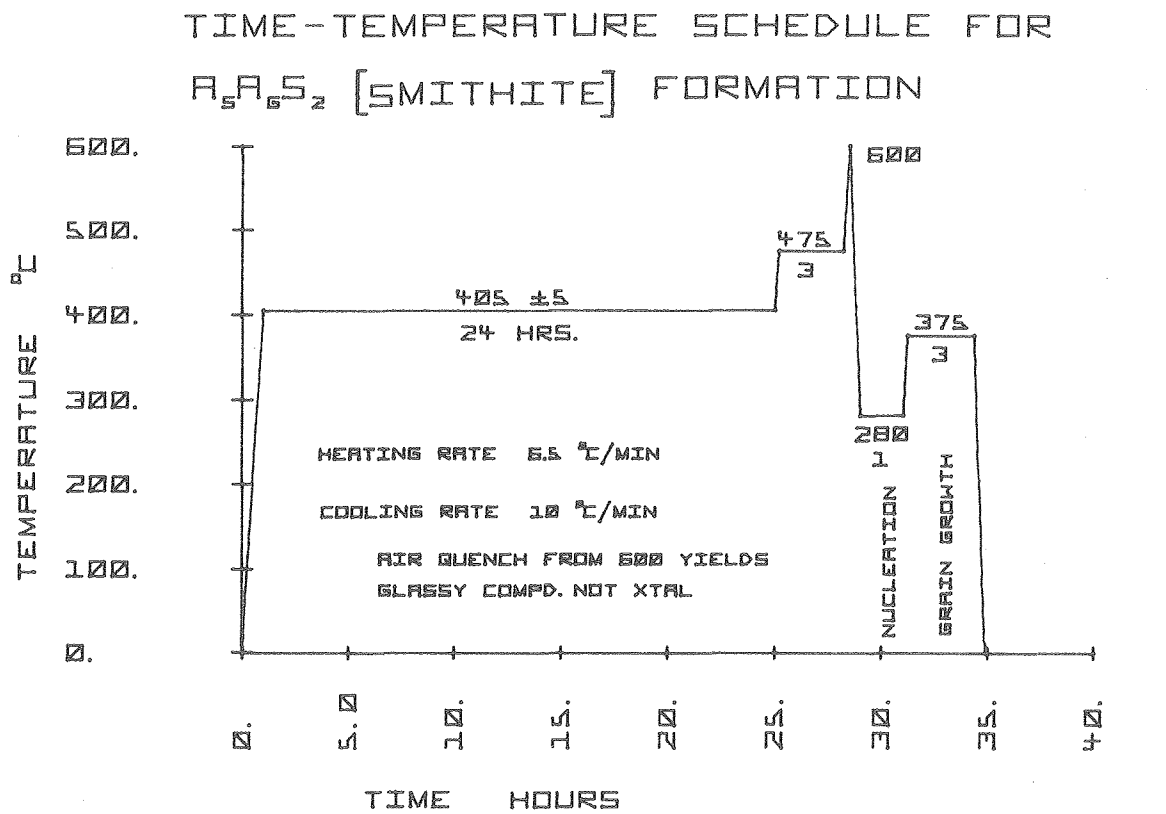
10. Sample 27 profile: Ag_2Se-As_2Se_3 couple, 30.8 hrs.

11. Sample 31 profile: Ag_2Se-As_2Se_3 couple, 25 hrs.

12. Sample 40 profile: Ag_2Se-As_2Se_3 couple, 12.3 hrs.

13. Microphotograph of condensation, Se islands and As containing pyramid.

14. Ag diffusivity vs. Ag concentration data for As chalcogenide glasses.



USING $A_{6_2}S$ POWDER PRESSED INTO CYLINDRICAL PELLETS 1 CM. HIGH AND 1 CM. DIAMETER

XBL 778-9882

Fig. 1

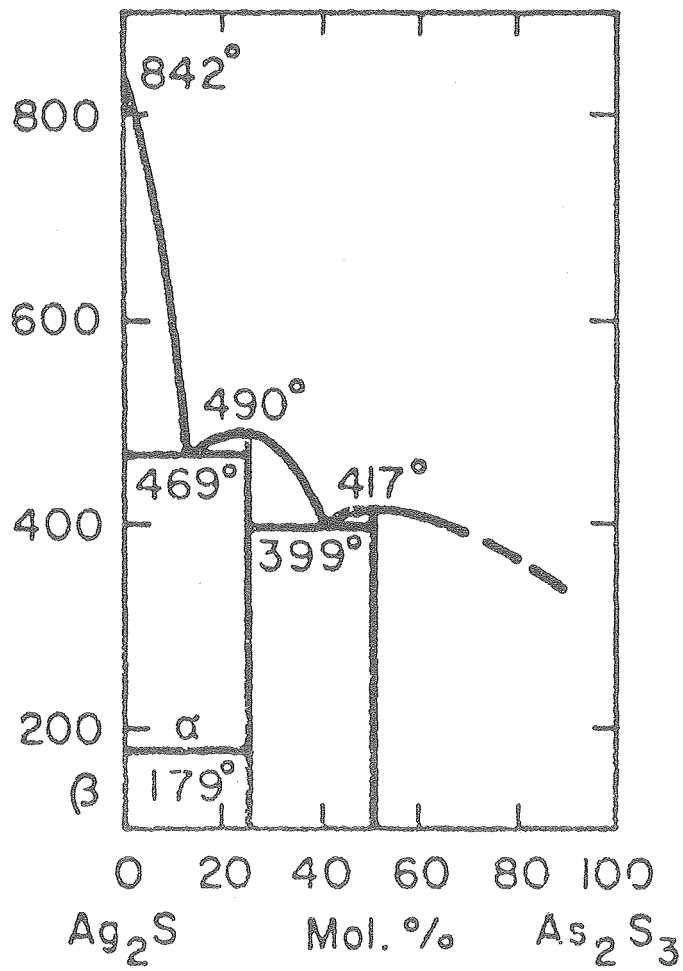


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Fig. 2

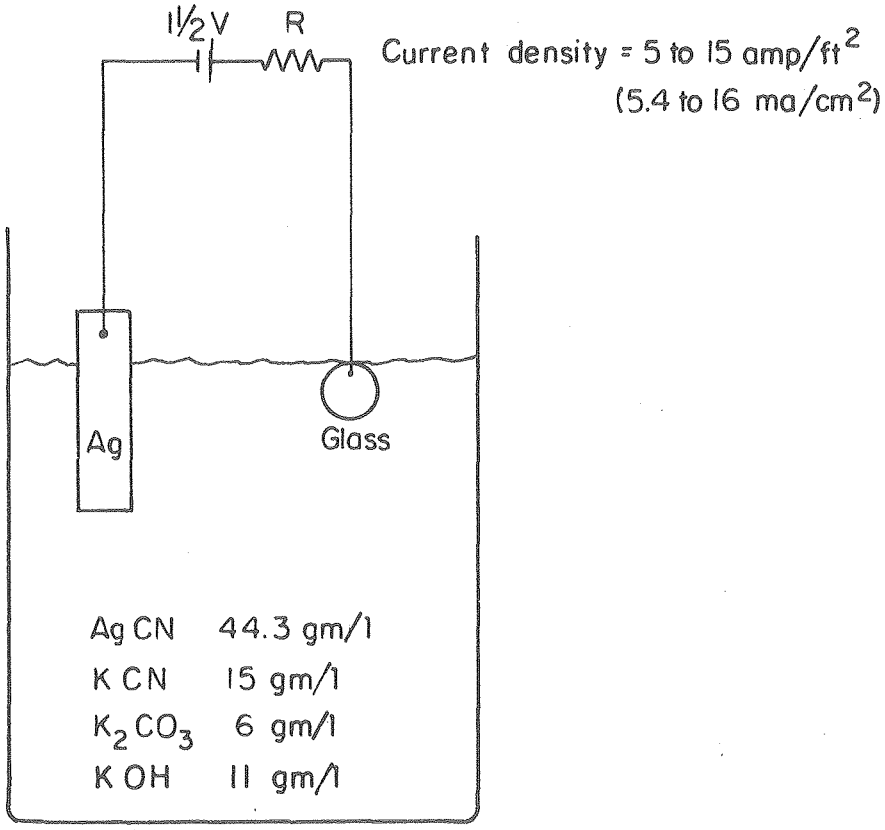

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Fig. 3

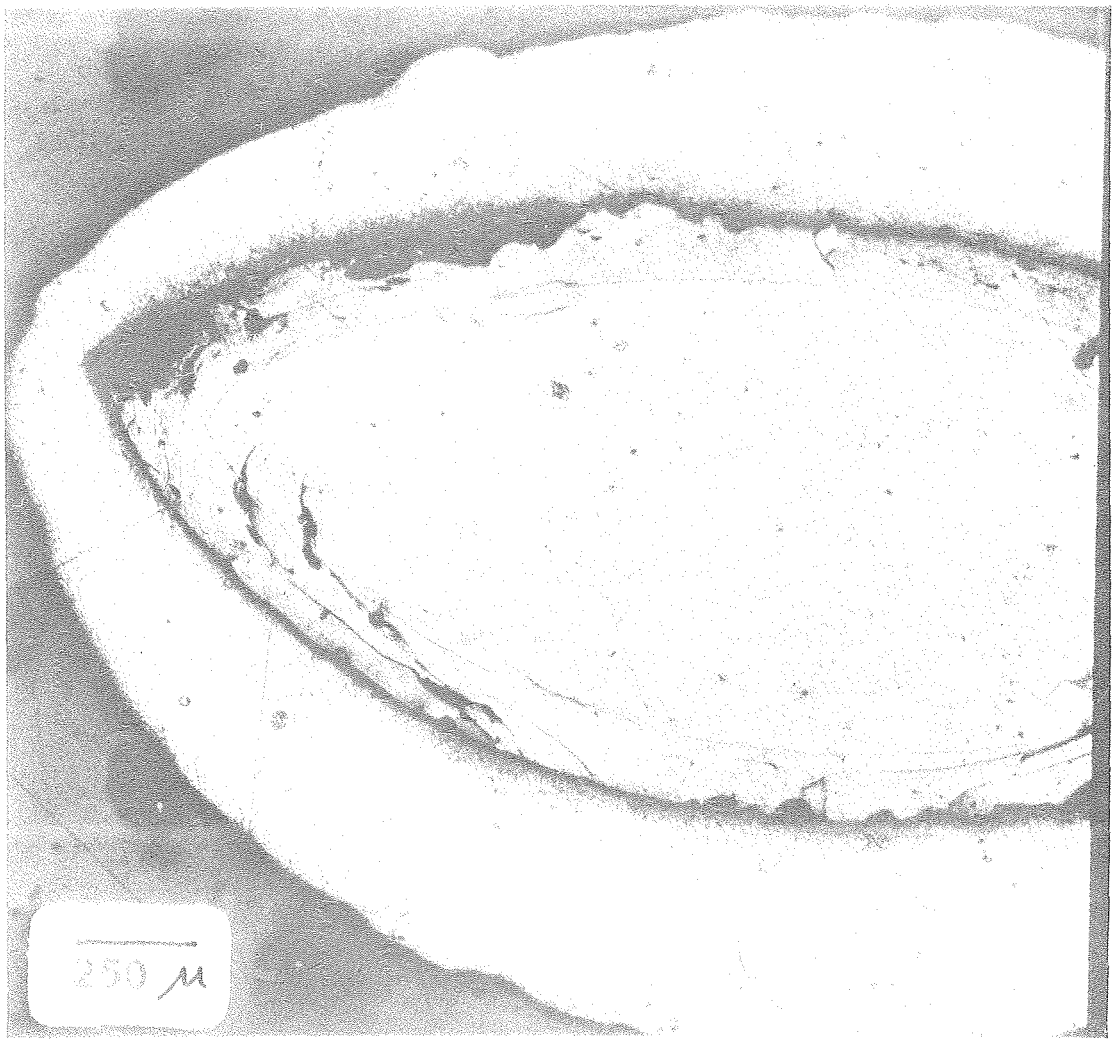

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Fig. 4

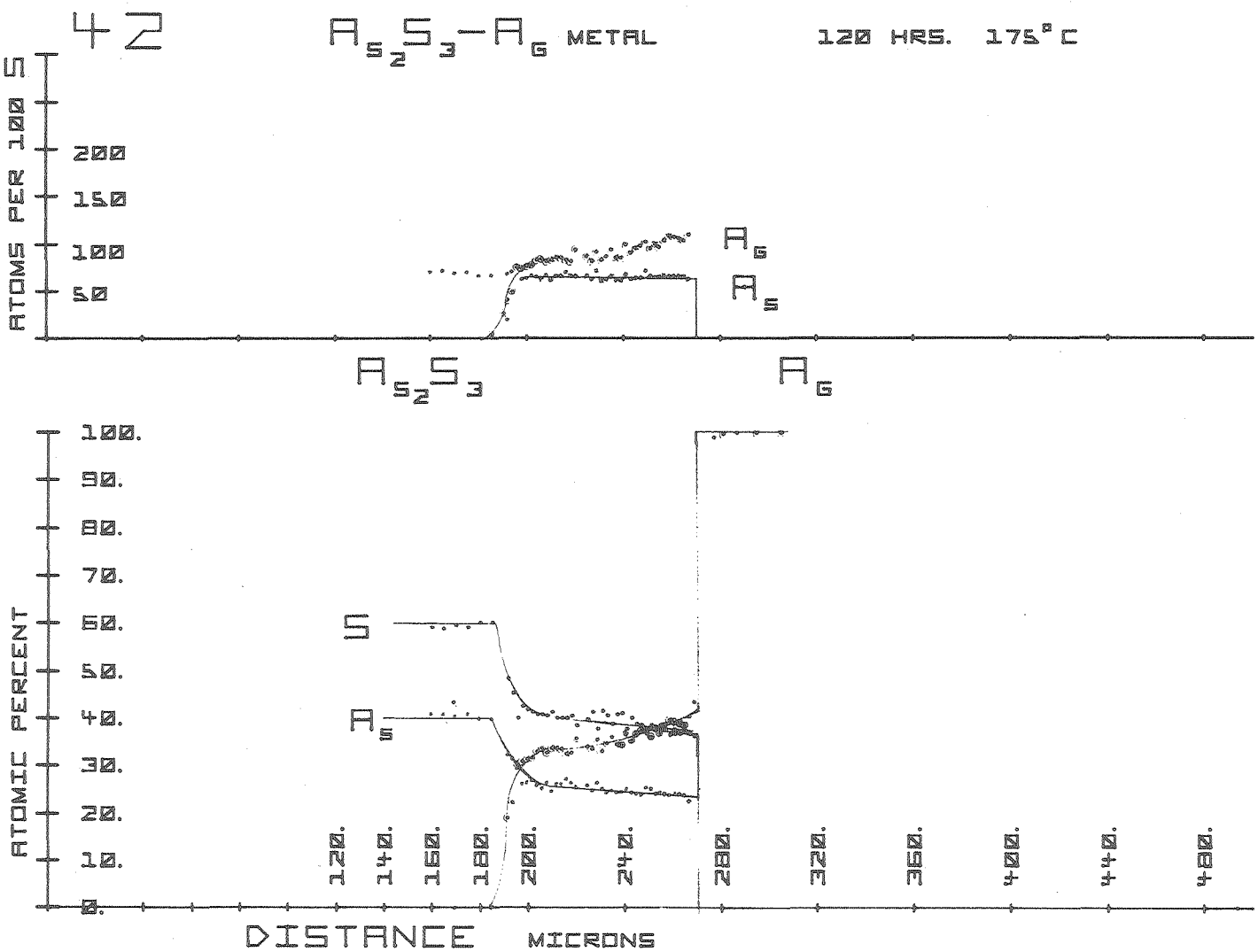

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Fig. 5

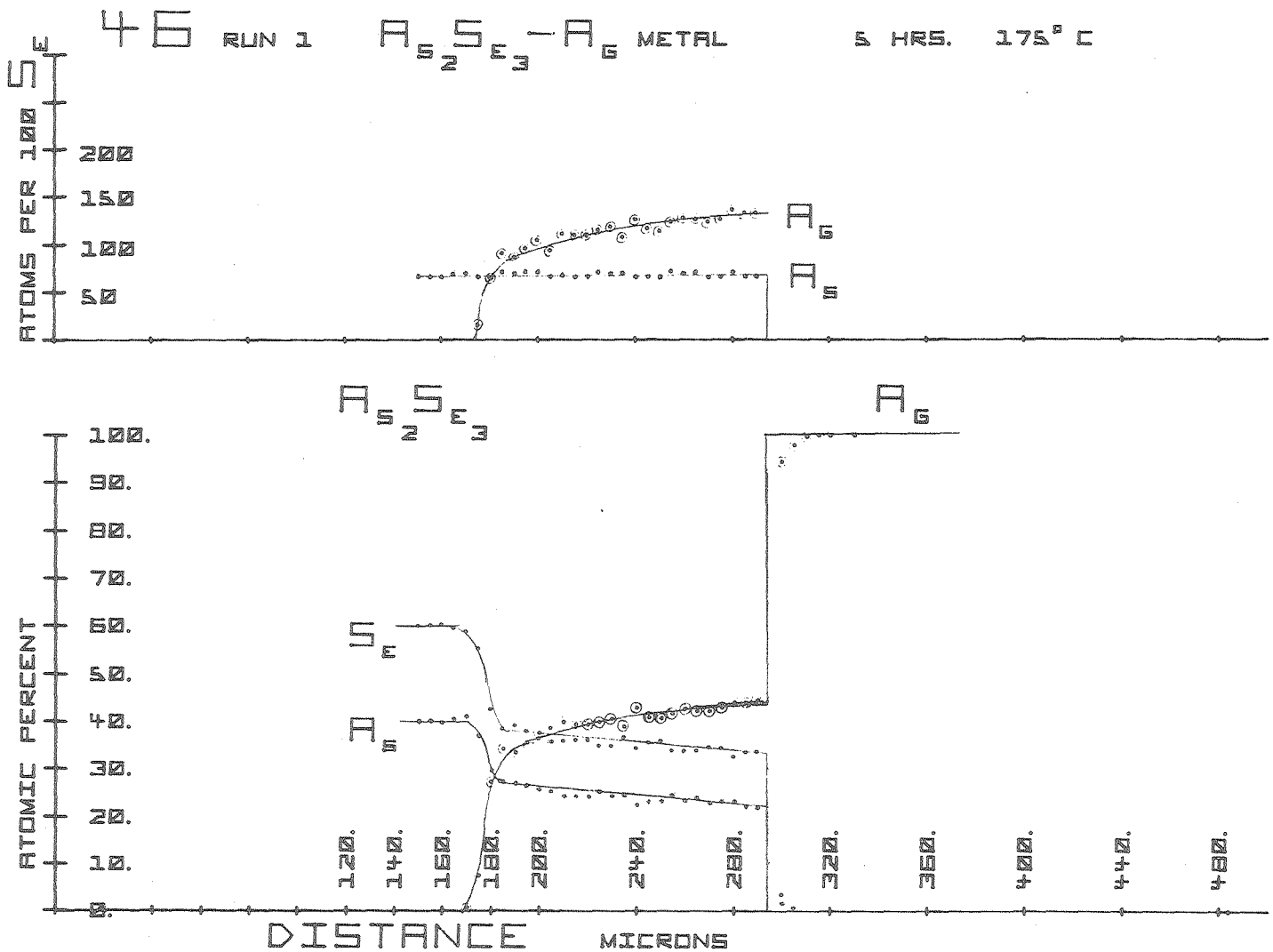

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Fig. 6

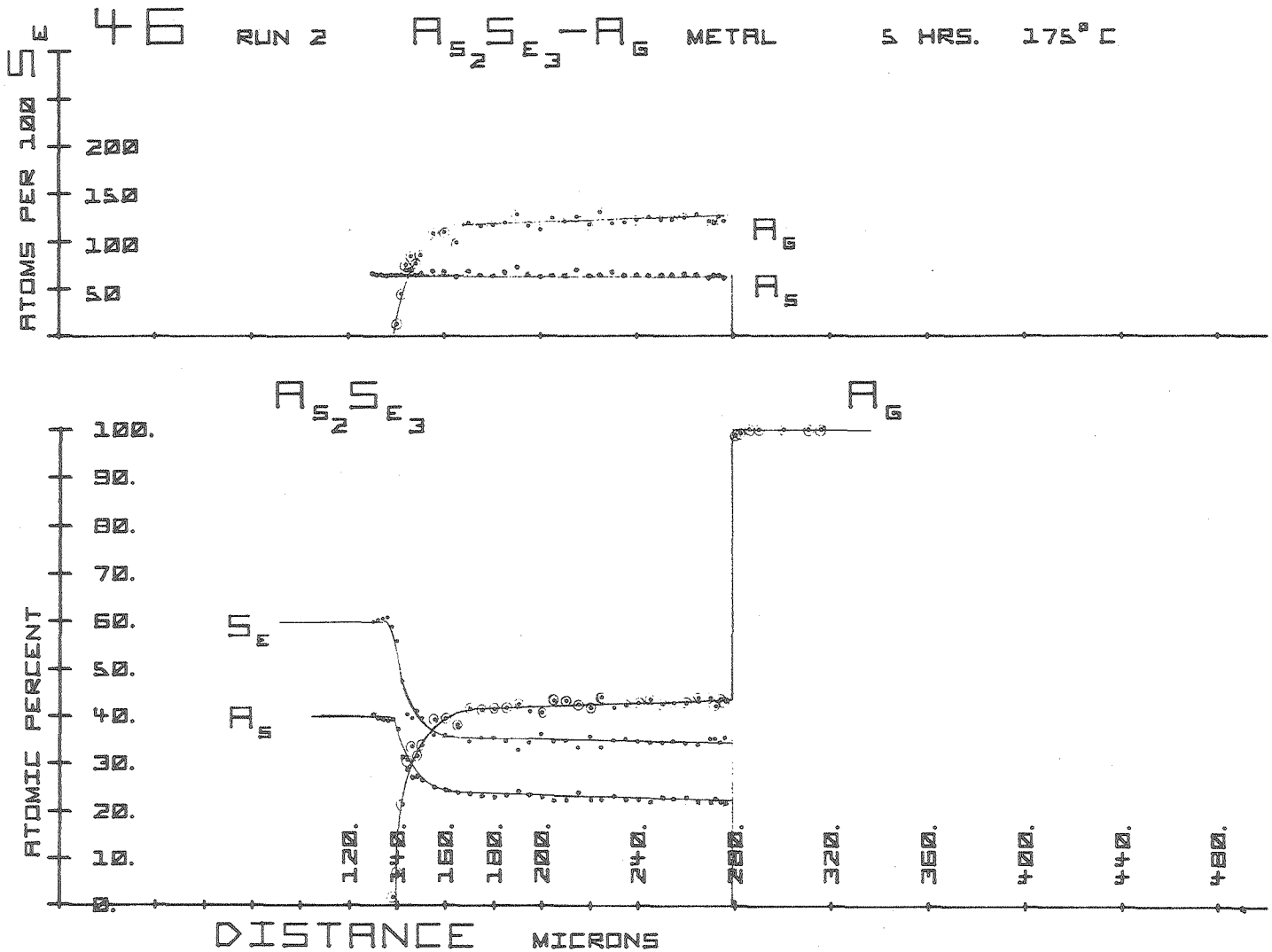

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Fig. 7

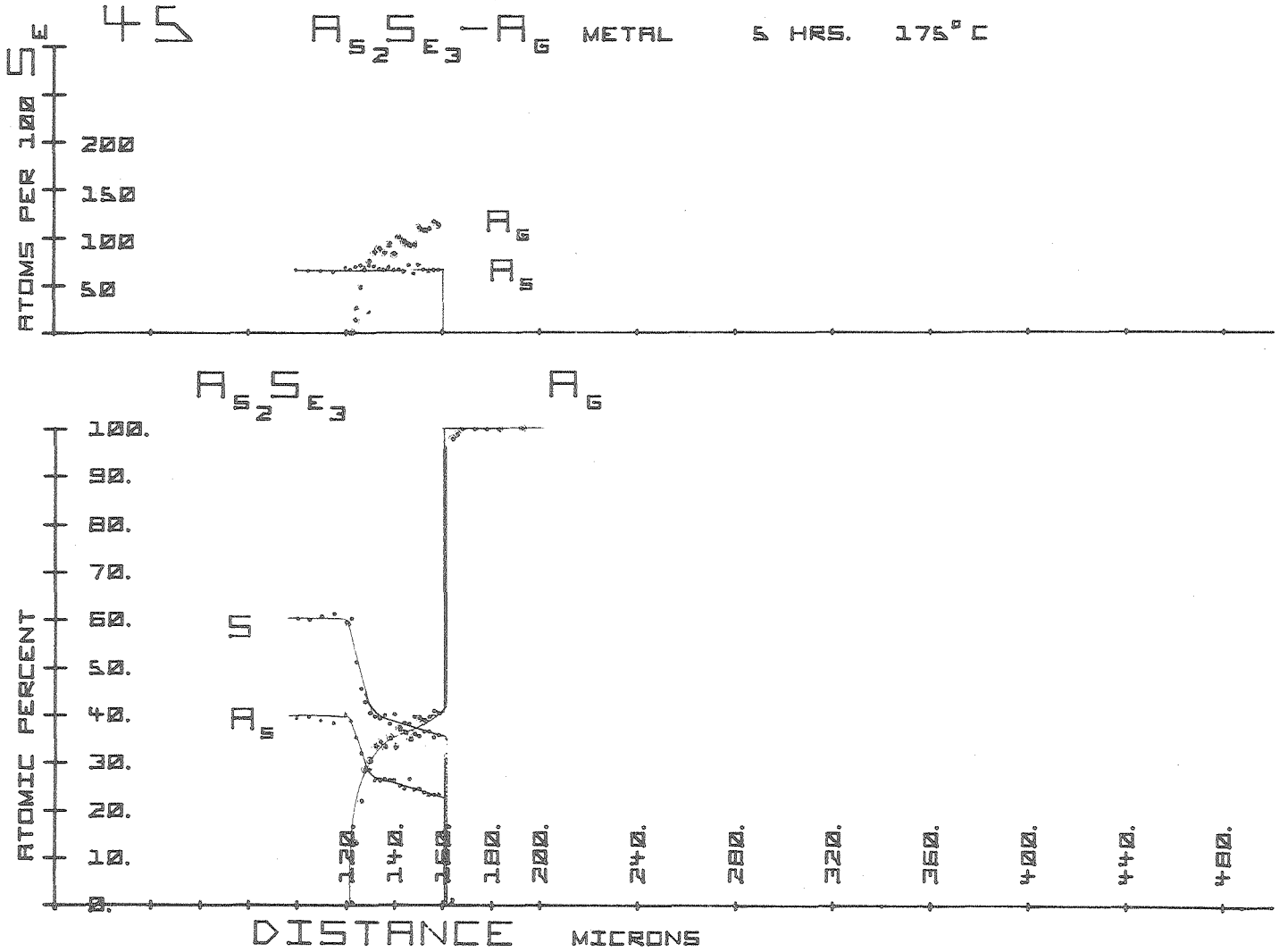

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Fig. 8

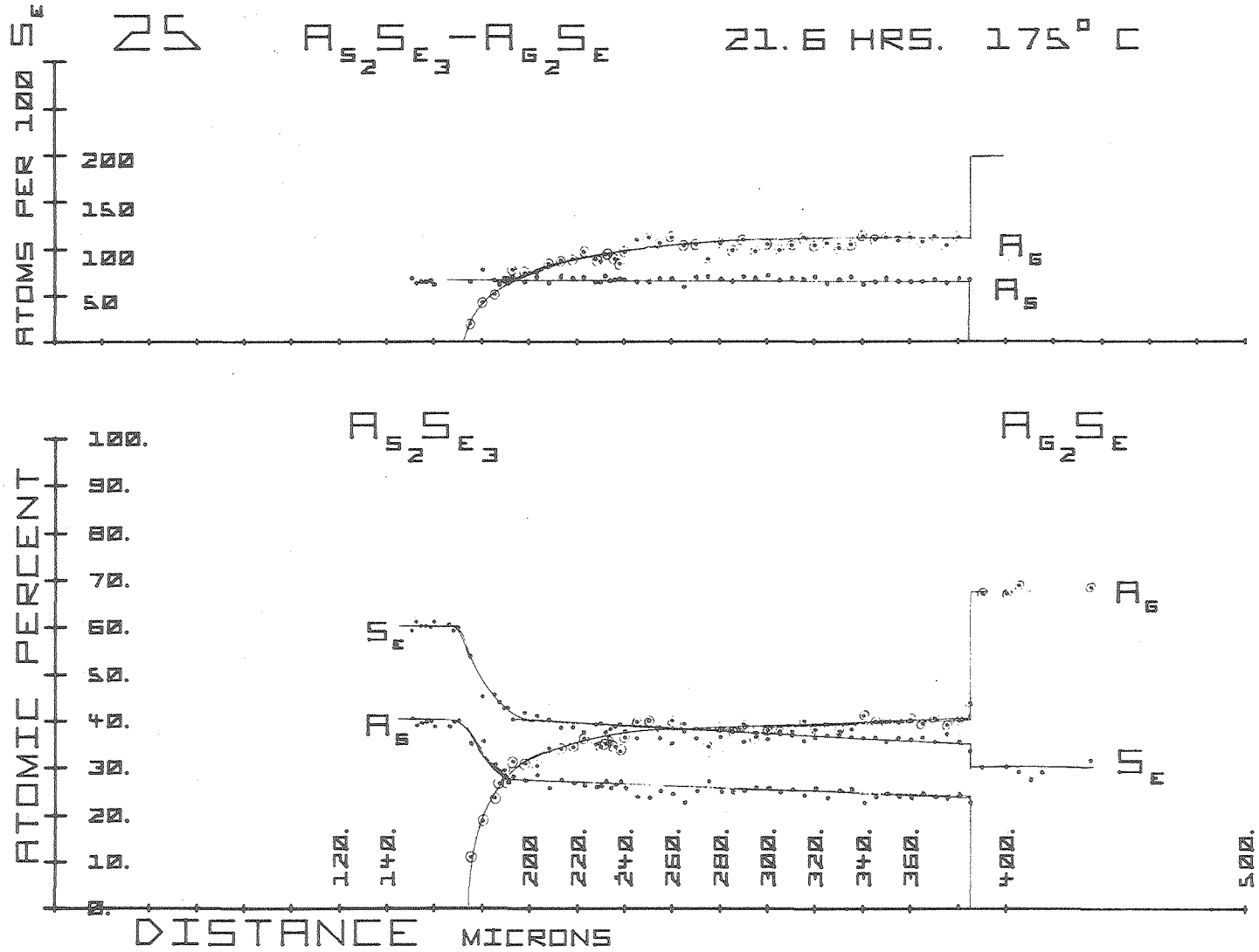

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Fig. 9

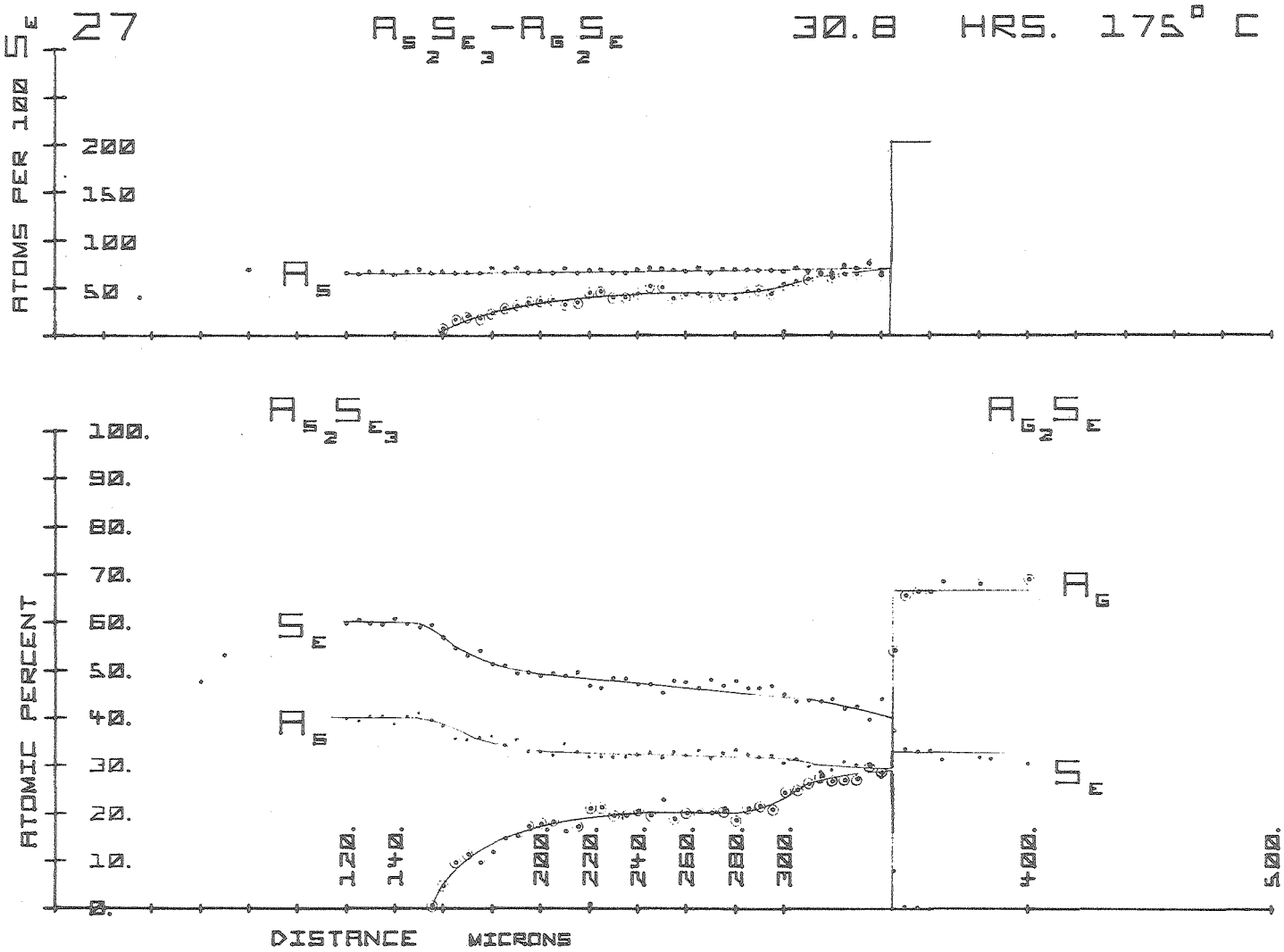

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Fig. 10

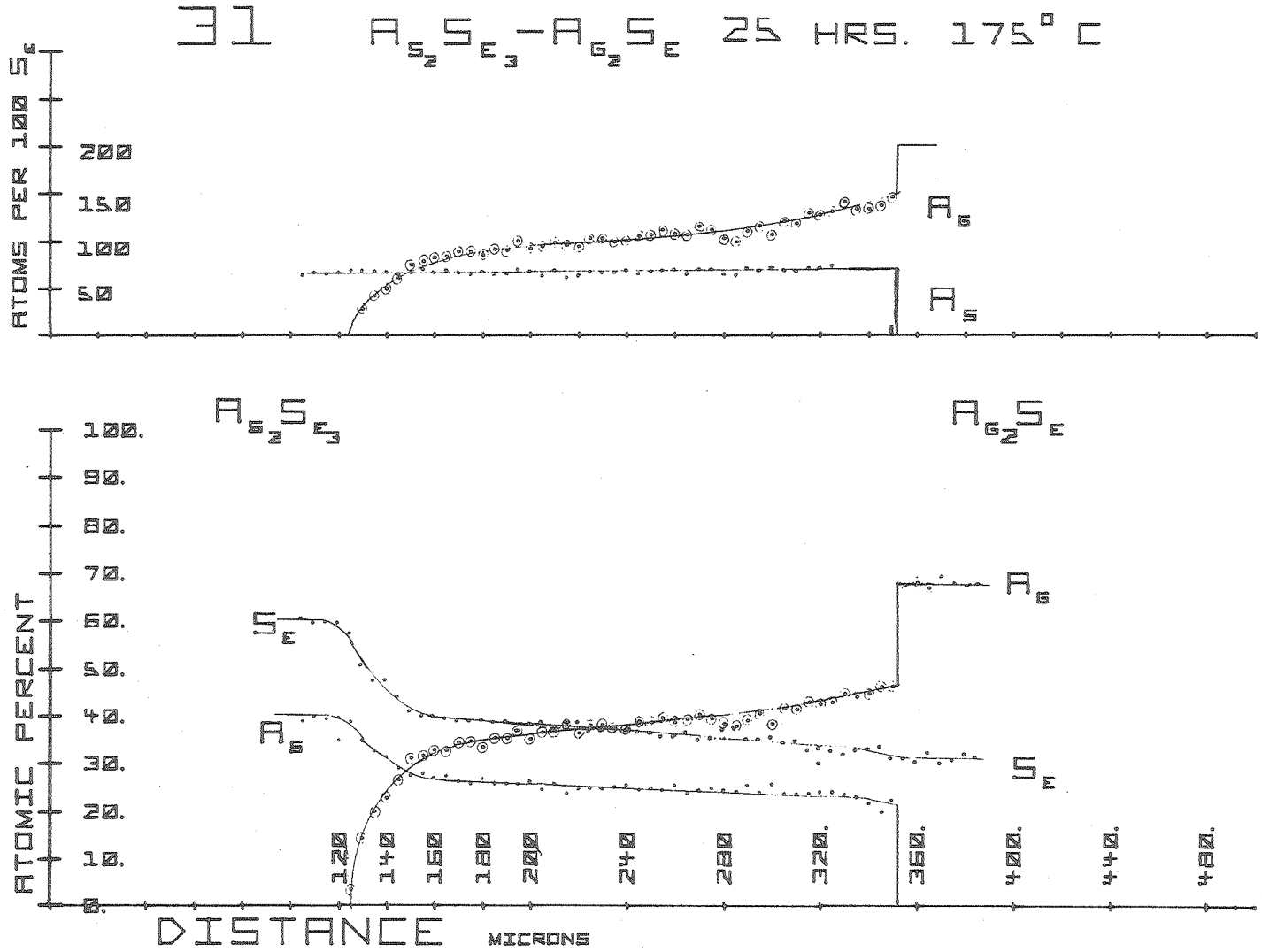

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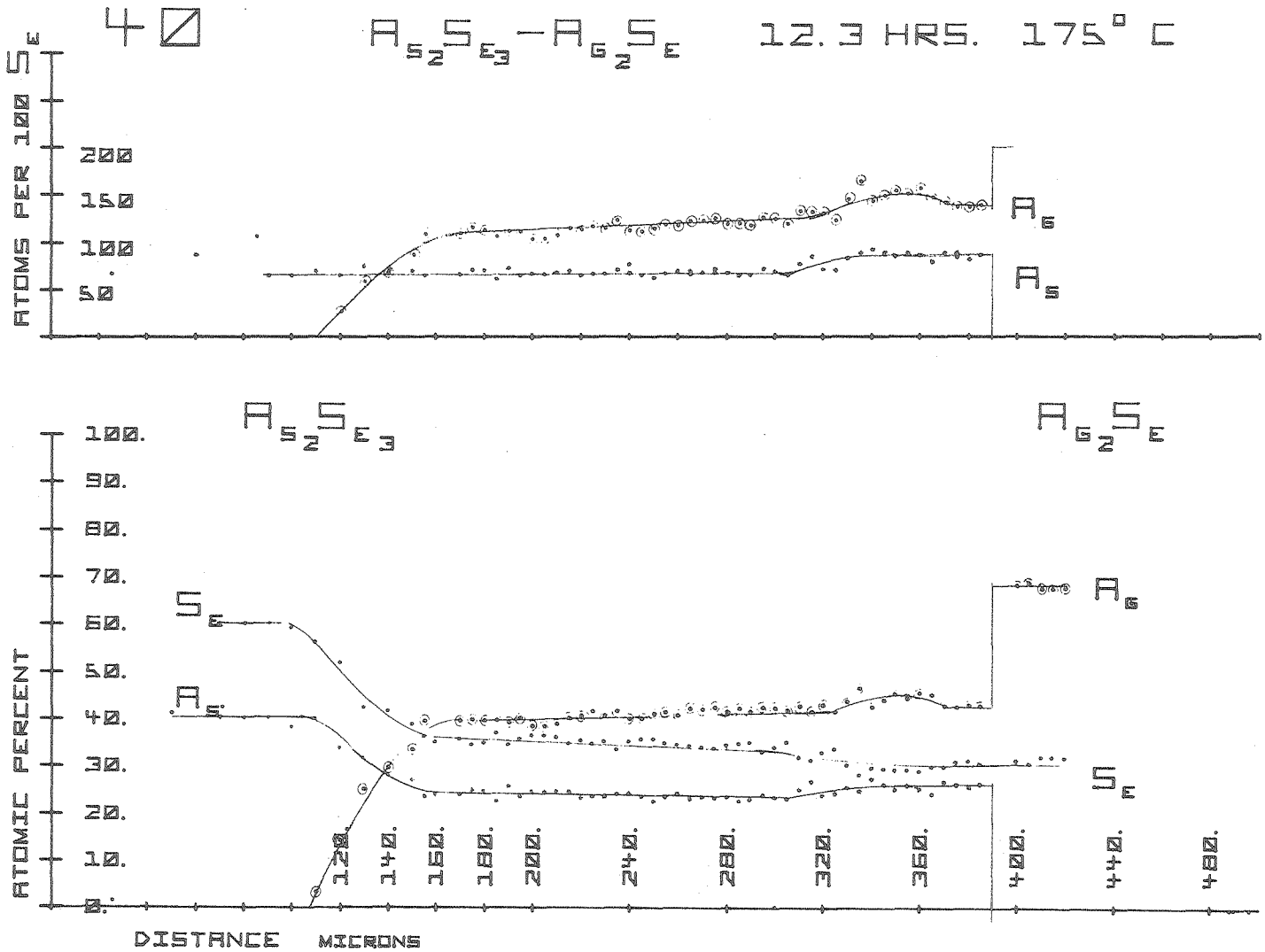
Fig. 11

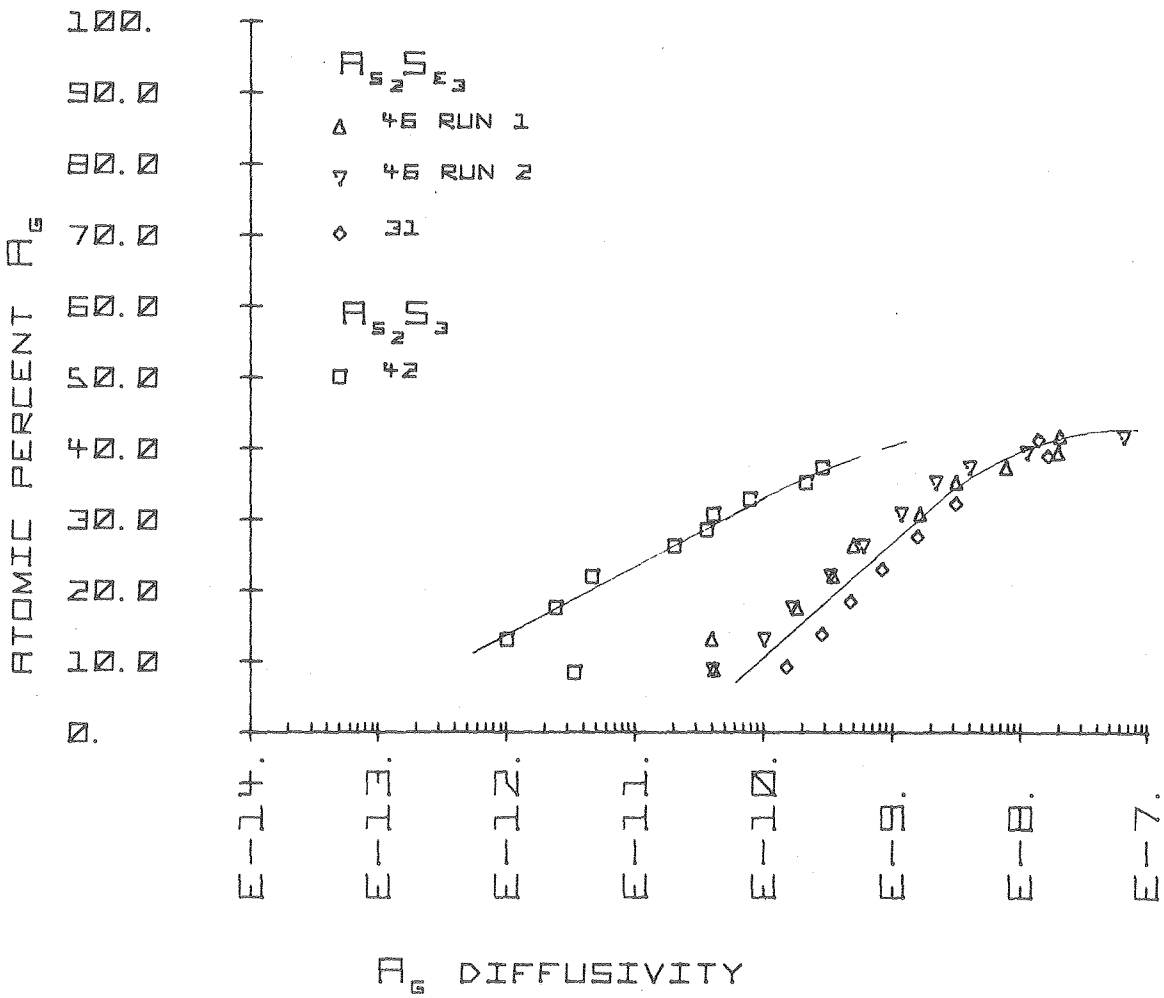


XBL 778-9893

Fig. 12

XBB777-6712

Fig. 13



XBL 778-9891

Fig. 14

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