

# An X-ray study by Guinier diffraction camera of Al-Ge alloys rapidly quenched from the melt

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Two Al-Ge alloys (6 and 30 at. % Ge) were levitation-melted and quenched in the rotary splat-quencher designed at Sussex University. X-ray diffraction patterns were obtained with crystal-monochromatized  $\text{CuK}\alpha_1$  in a precision Guinier camera, and further patterns were obtained after heating to various temperatures in a differential scanning calorimeter; the DSC was used to indicate when one of the metastable phases had completed its transformation. It was clear that there was more than one metastable phase in the concentrated (eutectic) alloy, possibly only one in the dilute alloy. Most of the lines matched those of the patterns reported by Rao *et al.* and by Köster; the agreement with Köster is very close, both as to lattice spacings and as to groupings of lines belonging to the different phases. Results published by other workers are completely at variance with ours. Köster's attribution of phases is confirmed by this study. (A recently developed iterative computer program was applied in an attempt to interpret the X-ray patterns *ab initio*, but was not found useful.) This study illustrates the difficulty of identifying metastable phases, especially when more than one is present, and points to the importance of using a high-precision X-ray diffraction technique.

## 1. Introduction

The aluminium-germanium equilibrium diagram features a simple eutectic at 30.3 at. % Ge and 697 K (Fig. 1). The maximum solubility of Ge in Al is 2.8 at. % at the eutectic temperature and that of Al in Ge is 0.97 at. % at 848 K [1].

A number of splat-quenching studies in the Al-Ge system covering the whole range of composition have been reported in the literature. Various investigators have reported extensions of primary solid solubility of Ge in Al and the formation of several metastable intermediate phases. Table I is an attempt to summarize the results of the several workers who have contributed to the literature on the splat-quenching of Al-Ge alloys.

Over the years a large number of apparently unrelated metastable phases have been reported in

the Al-Ge system over the same composition range on splat-quenching. Structures ranging from those with a cubic cell [2] to a complex monoclinic cell [3] have been assigned to the X-ray reflections from the splat-quenching products (apart from those belonging to the equilibrium Al and Ge). In addition, the formation of an amorphous phase in electron-transparent regions of a gun-quenched Al-30.3 at. % Ge alloy has been reported by Ramachandrarao *et al.* [4], who used an efficient diamond heat sink.

It has been suggested by several investigators, notably by Scott [5], that a possible reason for the remarkable discrepancies in the X-ray patterns and the nature of the phases attributed to them could be the lack of control over cooling rate, which may vary by several orders of magnitude

TABLE I Non-equilibrium phase formation in the Al-Ge system according to various investigations

Alloy composition (at. % Ge)	Splat-quenching technique	Techniques of examination	Solid solubility limit cited (at. % Ge)	Metastable intermediate phases reported	Reference
Al-30 Ge	Gun	Debye-Scherrer camera	Not quoted	Complex non-equilibrium phase reported	Predecki <i>et al.</i> [14]
Al-30 Ge	Gun	Debye-Scherrer camera	7 at. % Ge	Two cubic phases: $a = 1.287$ and $1.381$ nm	Salli and Kushnereva [2]
Wide range of com-	Gun	Debye-Scherrer camera	7.2 at. % Ge	Two tetragonal phases: $\gamma_1$ ( $a_1 = 1.291$ to $1.311$ nm $c_1 = 1.200$ to $1.210$ nm) $\gamma_2$ ( $a_2 = 1.498$ nm $c_2 = 1.603$ nm)	Suryanarayana and Anantharaman [8]
Al-8.5, 27 & 40 Ge	Gun	Diffractionmeter and Guinier camera	Not quoted	Rhombohedral ( $a = 0.765$ nm and $\alpha = 96.5^\circ$ ) Monoclinic ( $a = 0.6734$ , $b = 0.5818$ $c = 0.4282$ nm and $\beta = 88.96^\circ$ )	Köster [3]
Al-14.5 Ge	Piston and Anvil	Diffractionmeter	13 at. % Ge	A number of reflections belonging to metastable phases listed. No unit cell assigned.	Predel and Schluckebier [12]
Al-33 Ge	Gun	Debye-Scherrer camera and differential thermal analysis	7 at. % Ge	Two tetragonal phases: $\delta_1$ ( $a_1 = 0.659$ nm, $c_1 = 1.201$ nm) $\delta_2$ ( $a_2 = 0.625$ nm, $c_2 = 0.944$ nm) $\delta_1$ decomposes to an h c p phase, $\delta_3$ ( $a = 0.288$ nm, $b = 0.458$ nm) on heating.	Ramachandrarao <i>et al.</i> [10]

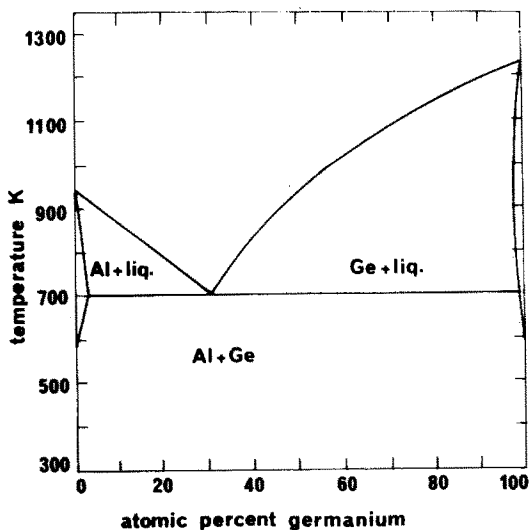


Figure 1 The Al-Ge equilibrium diagram (from Elliott [1]).

between rapid quenching apparatuses and in many cases even within one splat-quenched foil. The present study is an attempt to look more closely into non-equilibrium phase formation in the Al-Ge system using alloys of various compositions and three different splat-quenching techniques. In

particular, a new study was thought worthwhile because of our experiences with the application of a Guinier X-ray camera to splat-quenched alloys. The resolution of this camera is superior to that of a Debye-Scherrer camera [6] and the use of this camera was the *raison d'être* for the present study.

## 2. Experimental

The alloy compositions and the quenching techniques used are listed in Table II. The "gun" is a standard Duwez atomizing device; the "rotary splat-quencher" (RSQ) [7] is a device for breaking up a falling drop with high-speed rotating vanes

TABLE II Details of experimental techniques, substrate materials and alloy compositions for the splat-quenching of Al-Ge alloys

Quenching technique	Substrate	Alloy compositions examined (at.% Ge)
Gun: in argon	(i) copper (ii) diamond	Al-2, 4, 6, 8, 10 and 30.3 Ge
Rotary splat-quencher: in vacuum	copper	Al-6, 10 and 30.3 Ge
Two-piston technique: in vacuum	copper	Al-10, 30.3 and 60 Ge

and throwing the drop against a surrounding copper substrate: this device is almost as efficient as the gun. The two-piston device is an improved high-speed instrument relying on electromagnetic acceleration of the pistons [7]. All the splats were obtained under identical substrate conditions (grit-blasted) so that the splat-quenched structures obtained were essentially determined only by the quenching capabilities of the different instruments. Most of the observations reported here have been made with the RSQ.

The following techniques of examination were used to study the quenched products:

(i) *The Debye-Scherrer technique.* A single foil of the rapidly quenched material of the minimum bulk thickness obtainable from the gun or RSQ techniques was glued to the top of a 0.3 mm Lindemann glass capillary and exposed to the X-ray beam.  $\text{CuK}\alpha$  radiation was used at 35 kV, 20 mA, the exposure periods ranging up to 30 h. At a later stage the Debye-Scherrer technique was abandoned in favour of the more sensitive Guinier camera.

(ii) *The Guinier technique.* A fine-focus high-intensity X-ray tube was used in conjunction with a single crystal monochromator and Guinier camera adjusted for the transmission mode, to study the splat-quenched foils. The camera/monochromator system, manufactured by Huber, has a particularly good resolution.  $\text{CuK}\alpha_1$  (35 kV, 20 mA) radiation was generally used; the monochromator was precise enough to allow  $\text{CuK}\alpha_2$  to be eliminated.  $\text{CrK}\alpha_1$  (40 kV, 12 mA) was at times employed in vacuum to view the low-angle region of the diffraction diagram with more care. Typical exposure periods were 3 h.

(iii) *Differential scanning calorimetry.* Thermal analysis was employed in conjunction with X-ray diffraction to enable phase identification and separation in splat-quenched foils. Samples of approximately 20 mg were sealed in aluminium pans and heated in a Perkin-Elmer (model DSC-2) differential scanning calorimeter using heating rates of 0.33 and 0.66  $\text{K sec}^{-1}$ .

### 3. Results and discussion

#### 3.1. Supersaturated solid solutions

Measurement of the lattice parameters of dilute solid solutions (such as those that occur in splat-quenched Al-Ge alloys) is made difficult by the smallness of the changes in interplanar spacings as the solute concentration varies. For accurate

lattice parameter measurements, an internal aluminium standard was used and the differences in peak positions of the (2 2 0), (3 1 1) and (2 2 2) reflections as between pure aluminium and the aluminium-germanium solid solution were measured by photometering the Bragg reflections. Since the Guinier camera could be used to obtain patterns from three different specimens on the same film, the effective camera radius in the region of interest was accurately measured by using  $34 \mu\text{m}$  quartz powder as a standard and this provided a further calibration. On the basis of the known spacings for pure aluminium, the lattice parameter of the supersaturated terminal solid solution in a two-piston quenched Al-30.3 at.% Ge alloy was found to be  $0.40547 \pm 0.00005 \text{ nm}$ . The estimated error is based on repeated measurements for the same reflection and the values of the lattice parameter obtained from the three reflections also lie within the same margin of each other.

There are conflicting reports as to the variation of the lattice parameter with at.% germanium. To obtain the metastable solid solubility limit, Suryanarayana and Anantharaman [8] used the extrapolation of a relationship obtained by Axon and Hume-Rothery [9] based on a study of equilibrium solid solutions, namely,

$$a_{\alpha} = 0.40495 + 0.000166 C_{\text{Ge}} \text{ (nm)},$$

where  $C_{\text{Ge}}$  is the concentration of germanium in at.%. This represents a sharp negative deviation from the linear join between the values of pure aluminium and pure germanium used by Scott [5]. (In fact, the lattice parameter of an imaginary fcc pure germanium crystal, obtained by extrapolating Axon and Hume-Rothery's line to 100% Ge, is 0.4215 nm, as compared to 0.566 nm for real germanium, which is diamond-cubic.) Indeed, since aluminium and germanium have different crystal structures, one cannot envisage why extended solubilities should follow a Vegard's law plot (i.e. a straight line joining the lattice parameters of the elements). That straight line can be called a *pseudo-Vegard's law plot*. The use of the two above methods, i.e. the empirical Axon/Hume-Rothery plot extrapolated, and the pseudo-Vegard's law plot, leads to entirely different values of retained solubility, and indeed even the highest solute contents obtained by applying the pseudo-Vegard law are only in the range 1 to 2 at.%, less than the equilibrium solid solubility at high temperatures. This plainly makes no sense, and we thus, *faute de*

*mieux*, abide by the extrapolated empirical relationship.

Scott [5] quotes his observed approximate parameter of  $0.428 \pm 0.005$  nm of gun-quenched Al-33 at.% Ge as evidence, taken in conjunction with the pseudo-Vegard's law plot, that *all* the germanium is in supersaturated solution. 0.428 nm is actually higher than the lattice parameter of pure (though imaginary) fcc Ge. Since Scott found that his thin foil regions gave only fcc lines, his findings suggest that Hume-Rothery and Axon's straight line must not be extrapolated too far.

In Table III, the amount of germanium in solid solution has been calculated using the X-ray data of various investigators, using Hume-Rothery and Axon's calibration. The amount of germanium retained in solid solution in aluminium, as claimed by the various investigators, varies from 7 at.% Ge [8] to a high but unquantifiable amount in electron-transparent regions of gun-quenched specimens [5, 10]. In a recent review, Suryanarayana and Anantharaman [11] have questioned the conclusion by Ramachandrarao, Scott and Chadwick [10], whose values of the lattice parameter were based on (unavoidably imprecise) electron diffraction measurements, that they had ~30 at.% Ge in solution. However, from a critical study of X-ray line profiles, a large range of solute concentrations of the solid solution within the same foil in gun-quenched specimens is known to exist [6]. Hence, extremely high supersaturations in electron-transparent regions of gun-quenched

specimens should not be precluded (although exact figures cannot be obtained). This finding is also consistent with amorphous phase formation as reported by Ramachandrarao *et al.* [4], in samples quenched on diamond substrates. Here again, the highly inhomogeneous nature of gun-quenched specimens meant that only the thinnest regions had been cooled fast enough to be amorphous.

For the very reasons outlined above, no lattice parameter measurements of gun- and RSQ-quenched specimens were undertaken. In addition to strain and particle size broadening of X-ray reflections, the wide range of solid solutions present within one splat-quenched foil give a range of lattice parameters, especially if the retained solubility is high [6]. Hence it is somewhat surprising that Suryanarayana and Anantharaman [8] report an accuracy of  $\pm 0.0001$  nm for their value of lattice parameter, which is the best one can obtain for a well annealed specimen with well resolved  $K\alpha$  doublets using the Debye-Scherrer technique. The inaccuracies inherent in the above method (which incidentally seems to have been used by most investigators who have contributed to the literature on the splat-quenching of Al-Ge alloys) make any close estimation of the amount of retained solute a useless task. The difference in lattice parameters between the value of 0.40615 nm reported by Suryanarayana and Anantharaman [8] (who used the gun technique of splat-quenching) and 0.40578 nm reported by Predel and Schluckebier [12] (who used a piston and anvil rapid-quenching device) is 0.00037 nm, which could easily be with-

TABLE III Estimates of solid solubility extension of Ge in Al from X-ray data

Reference	Alloy composition (at. % Ge)	Quenching technique	Lattice parameter of the Al-Ge solid solution (nm)	Concentration of Ge in Al (at. % Ge) using extrapolated equilibrium data (Axon and Hume-Rothery [9])
Suryanarayana and Anantharaman [8]	10	Gun	0.40615	7.2
Ramachandrarao <i>et al.</i> [10]		Gun	Not quoted	~7.0
Scott [5]	33	Gun	$0.428 \pm 0.005$ (by electron diffraction of thinnest regions)	?
Predel and Schluckebier [12]	14.5	Piston and anvil	0.40578	5.0
Present work	30.3	Two-piston	$0.40547 \pm 0.00005$	3.1

Figure 2 Guinier diffraction pattern of Al-30.3 at. % Ge Alloy, rotary splat-quenched.  $\theta$  range 1–37°.

in the margin of error in the lattice parameter for splat-quenched alloys, as measured by the Debye–Scherrer method.

The conclusion we arrive at, therefore, is that the Debye–Scherrer method is too inaccurate to give reliable lattice parameters, whereas the Guinier camera, when applied to highly inhomogeneous samples, shows clearly the presence of a range of parameters. Its great sensitivity is, therefore, “empty” when applied to such samples. However, the two-piston quenching technique does give more homogeneous samples and for these the Guinier camera gives very accurate results. A slight supersaturation, 3.1 at. % Ge, was found in an alloy containing 30.3 at. % Ge, quenched by the two-piston technique.

In our opinion, a reliable means of estimating the maximum solid solubility, achieved by a particularly rapid quenching technique in those cases where lattice parameters of the primary solid solution cannot be measured accurately enough, is to ascertain the alloy composition at which the metastable intermediate phases first became detectable. Predel and Schluckebier [12], for example, indicated that this occurred at about 9 at. % Ge for their piston–anvil quenched specimens and yet claim solid solubility extension of up to 13 at. % Ge. Splat-quenching of the entire range of compositions indicated in Table II by the three techniques has shown that metastable intermediate phases may be present even in an Al–2 at. % Ge alloy. The reflections due to the metastable phases in dilute alloys (2 and 4 at. % Ge) were not detectable using the Debye–Scherrer technique for normal exposure periods of 4 h, but were easily detectable using the Guinier camera. This underlines the importance of using the most suitable investigation techniques for metastable phase identification. The conclusion to be drawn from the present study is that even at the fastest quench rates obtainable, there are some regions of the foil containing less than 2 at. % Ge in solution, so far as can be judged from X-ray diffraction techniques. Only the two-piston technique gives a fairly uniform concentration, at only slight supersaturation. (Further studies are in progress to establish how the degree of compositional heterogeneity varies with experimental variables in the two-piston technique.)

### 3.2. Metastable intermediate phases

The presence of metastable intermediate phases in splat-quenched Al–Ge alloys was confirmed by the observation in X-ray patterns of a large number of reflections other than those attributable to the Al–Ge solid solution. Reflections due to the metastable phases were present at all compositions ranging from 2 to 60 at. % Ge in splat-quenched foils obtained by all the three techniques. In a splat-quenched Al–30.3 at. % alloy, for example, a total of 75 reflections were recorded in Guinier patterns, covering the angular range 1 to 37° ( $\theta$ ) (Fig. 2). In view of this complexity of the diffraction pattern, it is not surprising that the total number of reflections observed by the various investigators who have used the Debye–Scherrer technique [2, 8, 10] has been different. Consequently, different unit cells were assigned by these investigators depending on the reflections they observed.

The experiments reported below were done primarily with two alloys quenched in the RSQ, containing 6 and 30.3 at. % Ge. Supplementary experiments were done with gun-quenched alloys of various compositions. At the outset, it was apparent that more than one metastable phase was present in splat-quenched alloys of Al–30.3 at. % Ge, which showed a mixture of the reflections characteristic of the Al–2 at. % Ge and Al–60 at. % Ge alloys. Following the precedent set by Ramachandrarao *et al.* [10], who first applied thermal analysis to the separation of metastable phases, the procedure adopted to separate the reflections due to the different phases was as follows:

(a) All reflections belonging to the metastable phases in Al–2 at. % Ge and 6 at. % Ge were assumed to belong to one phase ( $\epsilon_1$ ). These were separated out from the rest of the lines from the Al–30.3 at. % Ge alloy. The subsequent annealing out of this phase in the differential scanning calorimeter proved this assumption to be right.

(b) On heating the samples in the differential scanning calorimeter, two distinct exothermic peaks (Fig. 3) were recorded for the Al–30.3 at. % Ge alloy at 455 and 570 K. Samples of Al–2 and 6 at. % Ge registered only the first peak. The Al–30.3 at. % Ge alloy was heated in the DSC and after traversing the first peak, the scan was interrupted at 520 K and the alloy cooled down to room tem-

TABLE IV Interplanar spacings of reflections due to metastable intermediate phases

Al-30.3 at. % Ge		Al-6 at. % Ge		Al-30.3 at. % Ge		Köster [3]	Ramachandrarao <i>et al.</i> [10]	
RSQ		RSQ		RSQ heated to		(Guinier Camera)	(Debye-Scherrer camera)	
$\bar{d}$ (nm)	Int.	$\bar{d}$ (nm)	Int.	520 K in DSC		$d$ (nm)	$\bar{d}$ (nm)	Int.
				(Guinier camera)				
				$d$ (nm)	Int.			
0.4393	40	—	—	0.4393	40	0.4402 **	0.4385 ++	w
0.3635	80	—	—	0.3636	75	0.3643 **	0.3630 +	m
0.3591	70	—	—	0.3589	72	0.3583 **	—	—
0.3444	30	—	—	0.3444	25	0.3451 **	0.3465 +	vw
0.3360	27	—	—	0.3361	25	0.3366 **	—	—
0.3300	52	0.3299	100	0.3299	vw	0.3307 *	0.3296 +	w
0.3214	28	0.3214	56	—	—	0.3221 *	0.3215 ++	m
0.3150	23	0.3148	41	—	—	0.3155 *	0.3142 ++	m
0.3086	6	—	—	—	—	—	—	—
0.3028	77	0.3029	15	0.3029	65	0.3051†**	0.3031 +	m
0.2911	87	—	—	0.2911	80	0.2915 **	0.2906 +	m
0.2796	14	0.2792	—	—	—	0.2800 *	0.2792 ++	w/m
0.2669	100	—	—	0.2670	100	0.2671 **	0.2664 ++	s
0.2514	6	0.2513	13	—	—	0.2516 *	0.2509 +, +++	w/m
0.2425	36	—	—	0.2425	30	0.2427 **	—	—
0.2406	6	—	—	0.2406	4	0.2406 **	0.2410 ++	vw
0.2391	6	—	—	0.2391	5	0.2391 **	—	—
0.2303	33	0.2302	72	0.2303	vw	0.2307 *	0.2300 +++	w/m
0.2273	16	—	—	0.2274	10	0.2274 **	0.2227 +	w
0.2164	4	—	—	—	—	0.2166 *	—	—
0.2140	60	—	—	0.2140	50	0.2141 **	0.2145 ++	m
0.2096	6	—	—	0.2095	4	0.2093 **	—	—
0.2009	30	0.2009	70	—	—	0.2002 *	0.1996 +	w
0.1970	58	—	—	0.1970	50	0.1973 **	—	—
0.1965	66	—	—	0.1965	58	0.1967 **	0.1966 +	m
0.1947	66	—	—	0.1947	55	0.1948 **	—	—
0.1933	53	—	—	0.1933	50	0.1935 **	0.1939 +	m
0.1915	5	—	—	0.1915	5	—	—	—
0.1908	21	0.1909	33	0.1908	vw	0.1909 *	0.1905 ++	w/m
0.1890	56	0.1890	100	0.1890	vw	0.1891 *	0.1885 ++	m
0.1876	3	0.1875	8	—	—	0.1878 *	—	—
0.1865	13	—	—	0.1865	15	0.1864 **	—	—
0.1841	9	0.1840	20	—	—	0.1842 *	0.1840 +	w
0.1822	4	—	—	0.1821	9	—	—	—
0.1792	15	0.1792	35	—	—	0.1793 *	0.1791 ++	w

Table IV continued

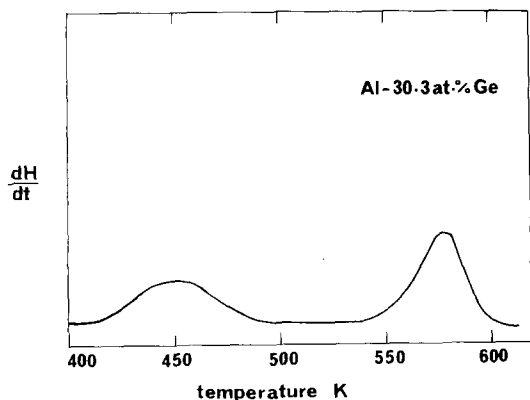


Figure 3 Typical DSC plot obtained from a splat-quenched Al-30.3 at. % alloy.

perature. Diffraction patterns obtained from this specimen recorded only the ( $\epsilon_2$ ) lines characteristic of the 60 at. % Ge alloy although, occasionally, faint reflections of the brightest lines of the metastable phase  $\epsilon_1$  were observed.

(c) The reflections present in the splat-quenched Al-60 at. % Ge alloy were measured and corresponded entirely to the metastable phase  $\epsilon_2$ , as identified in the experiment described in the preceding paragraph.

The results of the above experiment are presented in Table IV along with the  $d$ -spacings given by Köster [3] and Ramachandrarao *et al.* [10] for their metastable phases. (Köster used the two-piston quenching technique, while the other team used

TABLE IV Interplanar spacings of reflections due to metastable intermediate phases (*continued*)

Al-30.3 at. % Ge RSQ		Al-6 at. % Ge RSQ		Al-30.3 at. % Ge RSQ heated to 520 K in DSC (Guinier camera)		Köster [3] (Guinier Camera)	Ramachandrarao <i>et al.</i> [10] (Debye-Scherrer camera)	
<i>d</i> (nm)	Int.	<i>d</i> (nm)	Int.	<i>d</i> (nm)	Int.	<i>d</i> (nm)	<i>d</i> (nm)	Int.
0.1776	11	0.1776	25	—	—	0.1780 *	—	—
0.1767	26	0.1766	50	—	—	0.1761 *	—	—
0.1759	10	—	—	0.1759	10	—	—	—
0.1737	27	—	—	0.1738	30	0.1738 **	0.1736 ++	vw
0.1681	17	—	—	0.1680	18	—	—	—
0.1676	8	0.1675	18	—	—	—	0.1678 +++	w
0.1663	30	—	—	0.1663	32	—	—	—
0.1652	8	0.1652	18	—	—	0.1652 *	0.1658 +	w
0.1607	4	0.1607	10	—	—	—	0.1611 ++	w
0.1575	3	0.1575	6	—	—	0.1577 *	0.1574 ++	vw
0.1540	4	0.1540	9	—	—	—	—	—
0.1519	18	0.1519	37	—	—	0.1520 *	0.1518 ++	w
0.1502	2	—	—	0.1501	3	—	—	—
0.1483	2	—	—	0.1482	3	No further spacings available	—	—
0.1466	8	0.1467	17	—	—	—	—	—
0.1458	10	—	—	0.1458	10	—	—	—
0.1445	3	0.1444	6	0.1444	5	—	—	—
0.1420	3	—	—	0.1420	4	—	—	—
0.1408	11	—	—	0.1407	10	—	—	—
0.1399	9	—	—	0.1400	10	—	—	—
0.1391	3	—	—	0.1390	3	—	—	—
0.1375	8	—	—	0.1375	7	—	—	—
0.1371	15	—	—	0.1370	15	—	—	—
0.1361	6	—	—	0.1361	7	—	—	—
0.1351	18	—	—	0.1351	20	—	—	—
0.1334	5	—	—	0.1334	5	—	—	—
0.1310	13	—	—	0.1310	10	—	—	—
0.1288	15	—	—	0.1286	15	—	—	—
0.1278	4	—	—	0.1278	5	—	—	—
0.1273	8	—	—	0.1273	8	—	—	—

\*, \*\* =  $\gamma_1$  and  $\gamma_2$  (Köster [3]):  $\gamma_1$ , rhombohedral,  $a = 0.7672$  nm,  $\alpha = 96.55^\circ$ ,  $\gamma_2$ , monoclinic,  $a = 0.6734$ ,  $b = 0.5818$  nm,  $c = 0.4282$  nm,  $\beta = 88.96^\circ$ . +, ++, +++ =  $\delta_1$ ,  $\delta_2$  and  $\delta_3$  (Ramachandrarao *et al.* [10]).

† This is the only one of Köster's lines not to agree closely in position with one of ours.

gun-quenching.) No match could be obtained with the values reported by Suryanarayana and Anantharaman [8] or with those of Salli and Kushnereva [2]. In spite of the fact that we followed Ramachandrarao *et al.* [10] in the use of DSC as a separative device, their grouping of diffraction lines did not at all match ours.

It can be seen that the reflections present in the dilute alloy (6 at. % Ge) match well with the values reported by Köster\* for his metastable phase  $\gamma_1$  (found by him in alloys with 7 to 30% Ge) and the reflections left in the Al-30.3 at. % Ge alloy annealed to 520 K in the DSC with his phase  $\gamma_2$  (found by him in alloys with > 7% Ge, and identified as

AlGe). Occasionally, the brightest reflection of the metastable phase  $\epsilon_2$  ( $d = 0.2670$  nm) could be seen in the Al-6 at. % Ge alloy, which suggests that at solute contents greater than 6 at. % Ge both  $\epsilon_1$  and  $\epsilon_2$  co-exist (in accord with Köster's finding). This was also evident from the DSC experiments, where an Al-10 at. % Ge alloy occasionally gave the peak (570 K) due to the decomposition of the second metastable phase,  $\epsilon_2$ .

In addition to the two decomposition peaks observed in the present study, a low temperature peak at about 350 K was reported by Ramachandrarao *et al.* [10], which was attributed by these investigators to the decomposition of their first

\* A very few of Köster's lines are not matched by any of ours. They may have been very weak ones; he gives no information about this. The  $d$ -spacing match for out 0.3029 nm line is not very good.

metastable phase  $\delta_1$ . This peak was never recorded in the present study. Isothermal annealing of splat-quenched foils in evacuated Vycor tubes at 393 K for up to 48 hr showed that no decomposition of the metastable phases resulted on such a treatment. However, it was noticed that Ge came out of solid solution on heating the foils at 373 K for about 0.5 h. It is thus suggested that the first decomposition peak reported by Ramachandrarao *et al.* is due to the decomposition of the Al-Ge solid solution. No convincing reason can be advanced for its absence in the present study.

It was suggested in a recent publication [5] that the variation in quench rates obtained by the different splat-quenching techniques could account for the large differences in the results obtained by the various investigators. In fact, metastable constitution diagrams have been plotted by Suryanarayana and Anantharaman [8] and Ramachandrarao *et al.* [10] showing the dependence of the combinations of metastable phases formed on the cooling rates obtained. The present work, repeated using three different splat-quenching techniques estimated to give cooling rates between  $10^4$  to  $10^9$  K  $\text{sec}^{-1}$ , failed to bring out these differences if they existed at all. In all the cases, the same line positions due to the metastable phases were recorded.

After calculating the  $d$ -spacings of the reflections due to the two metastable phases,  $\epsilon_1$  and  $\epsilon_2$ , the problem next encountered was to allot unit cells to the two sets of reflections. It is here that a wide variety of structures have been assigned to the metastable phases, apparently over the same composition ranges. For precise structure determination it is necessary to have accurately measured  $d$ -spacings of the strongest reflections with low Miller indices. A rather difficult problem encountered achieving this in the Al-Ge system is illustrated in Fig. 4, which shows a strong reflection due to a metastable phase ( $d = 0.2009$  nm) almost overlapping the Ge (2 2 0) reflection; this strong reflection has for this reason apparently been missed by all investigators using the Debye-Scherrer technique, but was reported by Köster [3] who used a powder diffractometer, in conjunction with a Guinier camera for "exact structure determination". The Guinier camera is highly effective in revealing such "difficult" lines. Comparative photographs of the Debye-Scherrer and Guinier patterns of the

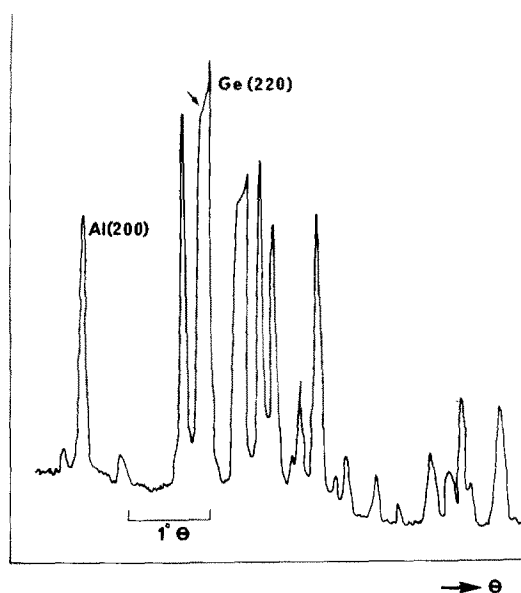


Figure 4 Part of a microdensitometer trace of a Guinier pattern from a splat-quenched Al-30.3 at. % Ge alloy, showing an (arrowed) reflection due to the metastable phase ( $d = 0.2009$  nm) almost coinciding with the Ge (2 2 0) reflection. The reflections are not clearly resolved.

same alloy show also how much more effective the Guinier camera is in revealing extremely faint reflections.

Only a few reflections attributable to the metastable phases were observed by Salli and Kushnereva [2]. For example, the indexing of their cubic unit cell starts with the (4 0 0) reflection, with the other low angle lines not reported. Although phase separation was achieved by using the DSC, the indexing of the metastable phase  $\delta_1$  by Ramachandrarao *et al.* [10] must be viewed with some doubt on account of the fact that the brightest reflection of the phase  $\delta_1$  (0.2339 nm) happens to fall on the (1 1 1) reflection of pure aluminium. Moreover, the reflection with  $d$ -spacing 0.2509 nm has been assigned to each of two metastable phases,  $\delta_1$  and  $\delta_3$ . The main puzzle, however, is the fact that their *grouping* of lines identified by them as belonging together is quite different from ours; yet both teams used the DSC in the same way.

The two sets of reflections in the present study agree well with the metastable phases  $\gamma_1$  and  $\gamma_2$  reported by Köster [3]\*. His diagnosis of the two unit cells (rhombohedral and monoclinic) was achieved by selected-area electron diffraction

\* The numerical agreement between our lattice spacings and those of Köster is closer than the agreement with those of Ramachandrarao *et al.*; this is not significant, since Köster had a Guinier camera and the others used the Debye-Scherrer method.



patterns. This method is open to considerable inaccuracies, but he was able to confirm that his *X-ray* line positions accurately matched those calculated on the basis of his provisionally identified cells. The only worry is that the metastable phase  $\gamma_2$  reported by Köster showed a heavily twinned structure, which would give rise to twin spots in electron diffraction patterns, making the reliable identification of a complex unit cell (monoclinic, with  $\beta$  close to  $90^\circ$ ) in electron diffraction patterns particularly tricky. Nevertheless, Köster's two unit cells do seem now to be effectively confirmed.\*

A major problem in identifying metastable phases in splat-quenched alloys is the separation of the X-ray reflections due to the various phases, especially where phases co-exist over a wide composition range, as in the Al-Ge system. A procedure commonly used is to observe the change in relative intensity with composition between different sets of reflections and then attempt to index each set self-consistently. This presumably was the method used by Suryanarayana and Anantharaman [8] since no differential thermal analysis was performed to enable phase separation. In view of the fact that no quantitative values for the intensities of reflections were given by these workers, it is difficult to see how the separation of the two sets of reflections they reported was achieved.

To help allot unit cells to the two sets of reflections separated in the present study, a computer programme due to Taupin [13] was used. For a set of "measured" *d*-spacings, this programme, by means of an iterative process, identifies a unit cell complete with its lattice parameters. Using the best value of the lattice parameters, it then "recalculates" the *d*-spacings of the unit cell. During the initial stages of using this programme, the *d*-spacings of the metastable phase reflections from a splat-quenched Al-10 at.% Ge alloy (known on the basis of a DSC experiment to contain a mixture of two phases) were fed into the computer which reported that *all* the lines could be attributed to a *unique unit cell* with a monoclinic structure. The computer programme was thereafter aborted. This underlines the dangers of trying to assign unit cells to sets of reflections that may or may not belong to a single phase. In view of this, the recent attempts of Suryanarayana and Anantharaman [11] to

rationalize the results of all the different investigators in terms of their proposed tetragonal structures arouse unavoidable scepticism.

#### 4. Conclusions

The principal conclusions that emerge from this study are that the utmost care is necessary in deducing supersaturations in splat-quenched alloys by X-ray diffraction and that the pitfalls are even greater in the deduction and identification of multiple intermediate phases. Short-cuts lead to invalid results and even very careful examination does not necessarily allow the identification of a unit cell.

It has been shown in the present investigation that the retained solubilities of germanium in aluminium estimated using X-ray diffraction techniques, as reported by several investigators, are a considerable overestimate. Most of the variation of values of the lattice parameters for a given alloy, reported by different users of the Debye-Scherrer technique, fall within the margin of error to which this technique is subject for splat-quenched alloys. The use of monochromatized X-rays<sup>†</sup> with a focusing camera, in conjunction with an internal standard method, has been found suitable for reliable estimates of the lattice parameter of solid solutions not very sensitive to the concentration of the solute, of which the Al-Ge system is an example; this is one of the principal conclusions of the present study. Even when the quenching technique does not give a homogeneous sample, a dominant lattice parameter can still be reliably measured so long as a substantial fraction of the sample is of uniform composition.

The apparent disagreement over metastable intermediate phase identification in the Al-Ge system stems from the failure to adopt the most appropriate investigative techniques and not, so far as we can judge, from a variation in cooling rates obtained by different investigators as had earlier been suggested. Two metastable phases,  $\epsilon_1$  and  $\epsilon_2$ , were identified in a splat-quenched Al-30.3 at.% Ge alloy by using differential scanning calorimetry in conjunction with Guinier X-ray diffraction. They appear to be identical to the rhombohedral  $\gamma_1$  and monoclinic  $\gamma_2$  phases identified by Köster. Köster's slow (two-piston) quench and our fast (RSQ) quench produced identical phases. It is no doubt

\* At the Second International Conference on Rapidly Quenched Metals, in November 1975, B.C. Giessen reported a monoclinic unit cell derived from X-ray analysis of small  $\gamma_1$  crystallites extracted from a splat-quenched alloy. Allowing for transformation of *a* and *c* axes, his unit cell appears to be the same as Köster's.

† Preferably with the  $K\alpha_2$  component removed, to avoid confusion at higher Bragg angles from overlapping  $\alpha$  doublets.

significant that Köster was the only other investigator to have used a Guinier camera.

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