Table 1. *Spacings of (hkl) lines of evaporated carbon film heated at* 1200 °C.

Values of d_c are calculated from graphite lattice having $a = 2·456$ Å. For comparison, positions of halos on diffraction pattern of carbon film without being heat-treated are also listed

$(s = 2\pi/d = 4\pi \sin \theta/\lambda)$

	Carbon film heated at 1200 °C.				Carbon film without being heat-treated
hkl	d_c (Å)	d_o (Å)	s_o (Å^{-1})	No.	s_o (Å^{-1})
(002)		3·408	1·84	1	1·2
100	2·127	2·120	2·96	2	2·9
(004)		1·71	3·67		
110	1·228	1·228	5·12	3	5·5
200	1·063	1·063	5·91		
210	0·804	0·8045	7·81		
300	0·709	0·7089	8·86	4	8·6
220	0·614	0·6135	10·2	5	10·4
310	0·590	0·5905	10·6		
400	0·532	0·532	11·8		
320	0·488	0·487	12·9		
410	0·464	0·4641	13·5	6	13·5
500	0·425				
330	0·409	0·409	15·4		
420	0·402	0·403	15·6		
510	0·382	0·381	16·5		
600	0·354	0·353	17·8		
430	0·350				
520	0·341	0·341	18·4	7	18·1
610	0·324				
440	0·307	0·305	20·6		
530, 700	0·304				
620	0·295				
710	0·282	0·281	22·4	8	22·4
540	0·272				
630	0·268	0·267	23·5		
800	0·266				
				9	24·8
				10	28·5
				11	32

lines can be observed. When the incident beam is normal to the surface of the film, the basal reflections (002) and (004) do not appear, but when the beam is inclined to the surface, they do appear as arcs which run across the vertical line as shown in Fig. 3. The interlayer spacing is estimated to be 3·41 Å. From these observations, it is obvious that films heated at higher temperatures have the random layer structure, each layer having orientation parallel to the film surface.

It is remarkable to note that the three-dimensional random network structure (composed of graphite-like and diamond-like configurations) of evaporated carbon film transforms into the random layer structure with prefered orientation at elevated temperature. The random layer structure is frequently found in the so-called 'amorphous' carbons, which are generally prepared by any heat treatment of about 1000 °C. and are known to transform into crystalline graphite at the higher temperature (1000 ~ 3000 °C.) with some exceptional cases (Franklin, 1951). The temperatures in the present treatment are comparable with those in preparation of other 'amorphous' carbons, and it is a future problem whether the obtained random layer structure will change to graphite crystal structure by further heat treatment or not. Extended study is now proceeding, and detailed analysis will be reported later.

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Comparison of three structure determinations for germanium selenide, GeSe.*

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The recent success at this laboratory in the preparation of high purity single crystals of germanium sulfide, GeS, and the subsequent optical and electrical measurements with these crystals prompted the continuation of similar measurements with other IV_b–VI_b compounds from these groups in the periodic table, especially those of germanium (Betz, 1958). It was found that germanium selenide, GeSe, could be prepared in a manner similar to that for GeS. A detailed description of the methods and techniques involved in producing high purity single crystals of GeS and GeSe is now in preparation and will be submitted soon for publication elsewhere.

At the beginning of this investigation only one previous publication by Ivanov-Emin (1940) had reported any work with solid GeSe. Preparation of the material, a few chemical properties, and a tentative crystal system assignment were given. Preliminary X-ray data obtained here were in disagreement with this Russian work, and therefore a complete structure analysis of GeSe was started in early 1958. When the present work was nearly completed a detailed structure analysis was reported by Okazaki (1958). Our results are in good agreement with those of Okazaki.

In Table 1, the complete disagreement with the Russian work is quite evident. In that determination, the crystal system and lattice parameters were deduced from only 18 powder photograph lines. The *d* values and intensities of these lines, with the possible exception of three or four, do not show any recognizable correspond-

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Table 1. *Comparison of the three* GeSe *structure determinations*

Author	Ivanov-Emin (1940)	Okazaki (1958)	Kannewurf *et al.* (1960)
Crystal system	Tetragonal	Orthorhombic	Orthorhombic
a (Å)	8·83 ± 0·02	4·38	4·40 ± 0·008
b (Å)	—	3·82	3·85 ± 0·008
c (Å)	9·76 ± 0·01	10·79	10·82 ± 0·01
Density (g.cm.$^{-3}$)			
ϱ (calc.)	5·266	5·57	5·49
ϱ (meas.)	5·30 ± 0·02	—	5·52 ± 0·03
Z (GeSe)	16	4	4
Space group	—	*Pcmn*	*Pcmn*
x_{Ge}	—	0·106	0·111 ± 0·004
x_{Se}	—	0·503	0·500 ± 0·004
z_{Ge}	—	−0·121	−0·121 ± 0·001
z_{Se}	—	0·148	0·146 ± 0·001
(y_{Ge} and y_{Se})	—	$\frac{1}{4}$	$\frac{1}{4}$
No. of reflections (all $\lvert F_o \rvert \neq 0$)	—	46	105
Reliability index (all $\lvert F_o \rvert \neq 0$)	—	0·18	0·15

ence with the data from the GeSe powder films obtained at this laboratory. Several of the *d* values and intensities do compare favorably with powder film data for the structures of the uncombined elements, especially that of germanium. However, there are still some lines listed with strong relative intensities, that definitely do not belong to the Ge, Se, or GeSe structures, for which there does not appear to be any obvious explanation. Thus, it is doubtful if the material investigated by Ivanov-Emin was pure GeSe. Also the agreement in experimental and calculated X-ray density is probably fortuitous since quantitative chemical analysis of small amounts of GeSe is somewhat difficult to perform accurately.

The lattice parameter values were determined at a temperature of 25 °C. from the highest angle lines obtained with a calibrated X-ray diffractometer. These values are a trifle larger in magnitude than those reported by Okazaki. The values given here are believed to be somewhat more precise as they are in better agreement with the identification of oscillation film reflections that occur very close to the limiting sphere in reciprocal space, in particular for the (0,0,14) and (4,0,10) reflections.

In the present work intensity data were obtained from oscillation films about both the *a* and *b* crystallographic axes. Because of the large number of (00*l*) and (0*kl*) reflections for which the intensities depend only on the *z* coordinates, tentative values for these coordinates were easily deduced. Therefore, the problem of obtaining the final values for all four coordinates could be much more easily prepared for solution on a digital computer by means of a grid point method than by the Fourier projection method. The values in Okazaki's work were determined from a (010) Fourier synthesis. In spite of the difference in the methods and the difference in the selection and number of reflections employed, the coordinate values from the two investigations appear to be in very good agreement.

The description of Wyckoff (1948) for the B29 structure type is well illustrated by GeSe. The GeSe structure is very similar to that of GeS as determined by Zachariasen (1932). In discussing the B29 structures Okazaki presents in his Table 5, a comparison of the atomic coordinates and objects to the *x* coordinates of GeS. However, he does not appear to have changed the origin of the GeS coordinate system to agree with the origin of coordinates presented for the other compounds. Hence the disagreement appears considerably greater than it actually is. Preliminary work on GeS here with oscillation films has confirmed Zachariasen's *y* coordinates to be correct within the limit of error originally given for them. A small change in the *x* coordinates is at present still possible; final values are yet to be determined, and further work is planned.

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