although (C) may be drived from (A) or (3), neither can be obtained from (C). Therefore, (C) is not equivalent to (3) and the comparison of (C) with (2) yields no information about the relative strengths of (2) and (3) or (2) and (A).

Zachariasen's paper

D_{HK} as defined in (5) is not the same as D_{HK} in (4). If (5) were labelled $D_{2H,2K}$ or, what is equivalent, if all the angles in (5) were divided by two, (4) and (5) would be in agreement. Furthermore, (5) would then be valid only for the case in which $S_H = S_K$. When $S_H = -S_K$, the cosine terms must be replaced by sine terms.

In an analysis of the averaging process to find $\overline{D_{HK}}$ one should first eliminate terms for which $j = k$ since the determinant is obviously zero in this case. Then, for $S_H = S_K$, (using $\sum\limits_{1}^{\frac{1}{2}N}{}'$ to indicate that the terms with $j = k$ are omitted) after expansion and using appropriate trigonometric identities,

$$\begin{aligned} D_{HK} = 4 \sum_{1}^{\frac{1}{2}N} \sum_{1}^{\frac{1}{2}N}{}' n_j n_k [& 1+\cos (\mathbf{H}+\mathbf{K}).\mathbf{r}_j + \cos (\mathbf{H}-\mathbf{K}).\mathbf{r}_k \\ & +\cos (\mathbf{H}+\mathbf{K}).\mathbf{r}_j \cos (\mathbf{H}-\mathbf{K}).\mathbf{r}_k - \cos \mathbf{H}.\mathbf{r}_j \cos \mathbf{H}.\mathbf{r}_k \\ & -\cos \mathbf{H}.\mathbf{r}_j \cos \mathbf{K}.\mathbf{r}_k - \cos \mathbf{K}.\mathbf{r}_j \cos \mathbf{H}.\mathbf{r}_k \\ & -\cos \mathbf{K}.\mathbf{r}_j \cos \mathbf{K}.\mathbf{r}_k] \,. \end{aligned} \tag{D}$$

All terms except the first average to zero when the average is taken over all possible triplets **H** and **K**; the same is true for $S_H = -S_K$. This leaves

$$\overline{D_{HK}} = 4 \sum_{1}^{\frac{1}{2}N} \sum_{1}^{\frac{1}{2}N}{}' n_j n_k = 4 \sum_{1}^{\frac{1}{2}N} \sum_{1}^{\frac{1}{2}N} n_j n_k - 4 \sum_{1}^{\frac{1}{2}N} n_j^2 = 1-2\sigma^2 \,,$$

which may be compared with $\overline{D_{HK}} = 1$ in the original paper. This correction is minor, since $2\sigma^2$ is small compared with 1 for most crystal structures.

However, in finding $\overline{D_{K_i,H+K_i}}$ when averaging over all K_i we are faced with a different process. The substitutions to be made in (D) are $K=K_i$ and $H=H+K_i$. Inspection of these new terms in (D) shows that the third term, $\cos \mathbf{H}.\mathbf{r}_k$, will not average to zero; all others except the first will average to zero. Then, in this case

$$\overline{D_{K_i,H+K_i}} = 1-2\sigma^2+U_H-4 \sum_{1}^{\frac{1}{2}N} n_k^2 \cos \mathbf{H}.\mathbf{r}_k \,.$$

For the case in which $S_H = -S_K$, the signs of the last two terms are interchanged. When this value of $\overline{D_{K_i,H+K_i}}$ is used in (9) it is found that

$$\begin{aligned} \overline{(|U_{K_i}|+|U_{H+K_i}|)^2} = 2\sigma^2 & \\ +\overline{S_{K_i}.S_{H+K_i}(U_{H+2K_i}}+4 \sum_{1}^{\frac{1}{2}N} n_k^2 \cos \mathbf{H}.\mathbf{r}_k) & \\ +U_H.\overline{U_{H+2K_i}} \,. & \end{aligned} \tag{E}$$

Thus is seems that Zachariasen's derivation cannot yield (11), the equation which is basic for the method.

Although these corrections show that the derivation is faulty, they give no information about the validity of the method. As Zachariasen points out, there is other less direct evidence supporting it, and his own success in the use of the method is more convincing than anything else.

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References

Grison, E. (1951). *Acta Cryst.* **4**, 489.
Karle, J. & Hauptman, H. (1950). *Acta Cryst.* **3**, 181.
Zachariasen, W. H. (1952). *Acta Cryst.* **5**, 68.

Acta Cryst. (1952). **5**, 847

The unit-cell dimensions and space groups of two modifications of crystalline glycylglycylglycine.*

By H. L. Yakel, Jr. and E. W. Hughes, *Gates & Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.*

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Three crystalline forms of the linear peptide glycylglycylglycine have been investigated previously. Of these, two, reported by Lenel (1932), are anhydrous; they are termed α- and β-glycylglycylglycine, while the third, studied by Bernal (1931), is an orthorhombic dihydrate. The unit-cell dimensions and space groups found by these authors are listed in Table 1.

In an effort to determine the complete crystal structure of one or more of these compounds, glycylglycylglycine prepared at the Harvard Medical School was recrystallized in these laboratories and X-ray investigations of the crystals were begun. Two distinct modifications were found in the preparations studied. One of these seemed to be identical with the α-glycylglycylglycine form but the other, probably a hemihydrate as shown by density measurements, had not previously been observed.

Accurate unit-cell measurements and density determinations on both crystal forms were made, with the results given in Table 2. Weissenberg and oscillation photographs were used to fix the space groups. The c axis obtained for α-glycylglycylglycine in the present investigation is just double the length reported by Lenel. This is probably due to the fact that insufficient data were collected in the earlier work, leading Lenel to overlook the possibility of a space-group extinction which would give only even orders of l in certain zones. The space group of the hemihydrate was not unambiguously fixed by the diffraction data, either Aa or $A2/a$ giving the observed extinctions. Piezoelectric or pyroelectric experiments to determine the polarity of the crystals have not been performed.

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* Contribution No. 1708 from the Gates and Crellin Laboratories.

Table 1.

Form	a (Å)	b (Å)	c (Å)	β	Z	Space group
α-Glycylglycylglycine	8·54	4·3	11·4	105·5°	2	Monoclinic
β-Glycylglycylglycine	14·6	4·80	11·69	105·5°	4	Monoclinic
Glycylglycylglycine dihydrate	22·0	9·8	4·7	90°	4	C_{2v}^5

Z = number of molecules per cell.

Table 2.

Form	a (Å)	b (Å)	c (Å)	β	Z	Density (g. cm.$^{-3}$)	Space group
α-Glycylglycylglycine	8·54	4·35	22·96	105°36′	4	1·57	C_{2h}^5
Glycylglycylglycine hemihydrate	16·04	4·64	24·99	112°43′	8	1·52	C_5^4 or C_{2h}^6

Several indications of the structure of the glycylglycylglycine molecules themselves can be deduced from the unit-cell dimensions in conjunction with data obtained with the polarizing microscope. In the case of α-glycylglycylglycine, it is likely that the peptide molecules are lying in an extended, or nearly extended, configuration parallel to the c axis. In the hydrated crystals, evidence seems to show that the peptide molecules are lying parallel to the $40\bar{6}$ plane. These elementary deductions are supported by Patterson projections for both modifications and although no entirely adequate trial structure for either crystal has been found as yet, the investigation is being continued.

The authors wish to take this opportunity to thank Dr E. J. Cohn of the Harvard Medical School for making available samples of glycylglycylglycine for this study.

References

Bernal, J. D. (1931). *Z. Krystallogr.* **78**, 363.

Lenel, F. V. (1932). *Z. Krystallogr.* **81**, 224.

Acta Cryst. (1952). **5**, 848

Crosses observed in the electron-diffraction pattern of an orientated CuAu film.

By Shiro Ogawa and Denjiro Watanabe, *The Research Institute for Iron, Steel and Other Metals, Tôhoku University, Sendai, Japan*

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In order to study the order–disorder problem of CuAu in the form of thin film, a film of orientated gold was first made by vacuum evaporation on a rocksalt cleavage surface heated at 400° C. Then copper was condensed on it at room temperature, the ratio of the thickness of the two films being so controlled that the double film was almost of the equi-atomic ratio of both atoms. After being detached from the rocksalt surface, this double film about 400 Å thick was homogenized at 350° C. for 1 hr., which was sufficient to complete the alloying of the two metals and to cause an ordering process; i.e. the electron-diffraction pattern showed an orientated f.c. tetragonal lattice after this treatment. When this alloy film was again annealed at a temperature immediately below the critical point, there appeared cross-like diffuse spots at some positions of superlattice reflexion in the diffraction pattern, as seen in Fig. 1(a). Patterns like this have been observed by several workers using X-ray methods; for instance, by Guinier & Griffoul (1948) in Cu_3Au and CuAu and by Newkirk *et al.* (1951) in the alloy CoPt. In the former case, the crosses appeared only at the superlattice reflexion positions, whereas in the latter the normal spots were converted into diffuse crosses. Therefore, our pattern belongs to the former type. Raether (1951) also observed the disc-like cross effect while studying Cu_3Au films by electron diffraction. In our case the crosses could be observed with comparative ease because of the greater intensity of the superlattice reflexion than in the case of Cu_3Au.

According to Guinier & Griffoul, the crosses can arise from the formation of anti-phase domains in the course of ordering, and the domain size can be calculated from the width of the cross. The thickness of an anti-phase domain thus calculated from our pattern was $4a$ in the direction of the a axis. According to Johansson & Linde (1936), such a lattice may be considered as orthorhombic. The ratio of the two axes perpendicular to the c axis, which could be determined with a polycrystalline alloy film* treated in the same way as the orientated film mentioned above, was 10, from which the thickness of an anti-phase domain of $5a$ resulted. The rough coincidence of the estimated values in both cases was thus obtained.

The condition of preparing the CuAu films was such that the (100) plane of an initially deposited orientated gold was parallel to the surface of the film, and in the homogenized alloy film the c axis was distributed in the directions of the three cubic axes of the gold. Therefore, in Fig. 1(a) a mixture of these orientations appears, which is illustrated by three kinds of marks in Fig. 1(b).

Fig. 2 shows a reciprocal lattice of CuAu containing anti-phase domains, cross-like platelets being indicated at the positions of superlattice reflexions as in the case of Cu_3Au (Guinier & Griffoul, 1948). In the ordered CuAu

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* A break-up of a superlattice reflexion arising from anti-phase domains has previously been observed in the (110) ring of the polycrystalline Au_3Cu film (Ogawa & Watanabe, 1951) annealed at 200° C. for 150 hr. This fact, however, was overlooked at that time.