

## X-ray study of ordered phase formation in $\text{Au}_{31.6}\text{Cu}_{68.4}$ , $\text{Au}_{50}\text{Cu}_{50}$ and $\text{Au}_{75}\text{Cu}_{25}$

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### Abstract

Ordered phase formation in  $\text{Au}_{31.6}\text{Cu}_{68.4}$ ,  $\text{Au}_{50}\text{Cu}_{50}$  and  $\text{Au}_{75}\text{Cu}_{25}$  alloys has been observed by X-ray diffraction methods. The results are compared and contrasted with the findings of several other studies on transformations in Au–Cu alloys. In general it is concluded that there is an increasing tendency towards separation of gold and copper atoms with decreasing temperature.

### 1. Introduction

The work described in this paper is a continuation of our earlier attempt [1] to study the process of ordering and formation of  $\text{AuCu}^{\text{II}}$  and  $\text{AuCu}^{\text{I}}$  phases in  $\text{Au}_{50}\text{Cu}_{50}$  alloy.

On the copper-rich side of the Au–Cu system the formation of  $\text{AuCu}_3^{\text{II}}$  and  $\text{AuCu}_3^{\text{I}}$  is known but is still not well understood. From the experimental data it is established that the limiting concentration for the long period superlattice (LPS) of  $\text{AuCu}_3^{\text{II}}$  type lies somewhere around 29–38 at.% Au [2–4]. In this work we choose the composition  $\text{Au}_{31.6}\text{Cu}_{68.4}$  in order to be able to compare our X-ray results with those of Scott [2]. In addition, we want to determine if there exists a cubic-to-tetragonal  $\text{AuCu}_3^{\text{II}}$  transformation for  $\text{Au}_{31.6}\text{Cu}_{68.4}$  as was found for  $\text{Au}_{35}\text{Cu}_{65}$  in 5.

On the gold-rich side of the Au–Cu system an ordered  $\text{Au}_3\text{Cu}$  phase is supposed to exist, but the structure has not been reliably analysed by X-ray diffraction [6]. Therefore we also seek to obtain more information on the origin of the  $\text{Au}_3\text{Cu}$  superlattice formation.

### 2. Experimental details

$\text{Au}_{31.6}\text{Cu}_{68.4}$ ,  $\text{Au}_{50}\text{Cu}_{50}$  and  $\text{Au}_{75}\text{Cu}_{25}$  alloys were prepared from appropriate amounts of gold (purity 99.9%) and copper (purity 99.99%) melted together in evacuated and sealed quartz tubes and then quenched in water. Next the ingots were converted into filings from which spherical crystals [7] for single-

crystal measurements and polycrystalline samples for powder measurements were prepared. A further heat treatment of the single crystals and powder samples was also performed in evacuated and sealed quartz or glass tubes. X-ray measurements were made at room temperature (besides thermal expansion measurements) using Cu  $K\alpha$  radiation.

$Au_{31.6}Cu_{68.4}$  crystals were inspected with a Weissenberg goniometer, a four-circle KM-4 diffractometer (KUMA-Diffraction, Wrocław, Poland) and a Bond diffractometer [8].  $Au_{31.6}Cu_{68.4}$ ,  $Au_{50}Cu_{50}$  and  $Au_{75}Cu_{25}$  powder samples were characterized on a Stoe transmission diffractometer [9] with a position-sensitive detector.

## 2.1. $Au_{31.6}Cu_{68.4}$

### 2.1.1.

TABLE 1

Data from X-ray photographs (Weissenberg goniometer)

Crystal no.	Annealing conditions		Observed diffraction effects
	Temperature (°C)	Time (days)	
1	850	1	Fundamental reflections only (from f.c.c. cell, $a = 3.782 \text{ \AA}$ )
2	800	1	Fundamental reflections + broad spots at positions of superlattice reflections (observed on overexposed photographs) – Fig. 1
3a	800	1	Fundamental reflections + weak, sharply focused superlattice reflections with satellite patterns separated by a distance reflecting LPS with cell $A_1 \approx 18a_1$ , $a_2 = a_3$ – Fig. 2
	340	14	
3b	270	82	Fundamental reflections + superlattice reflections
4	800	1	No qualitative differences in intensities of or separation distances between reflections in relation to crystal 3a
	340	14	
	200	56	

### 2.1.2. Data from four-circle KM-4 diffractometer

Crystal 3a was mounted on the four-circle KM-4 diffractometer and measured using the  $\omega$ - $2\theta$  scan technique and monochromated Cu  $k\alpha$  radiation. The fundamental reflections observed on the Weissenberg photographs have been confirmed, as has the presence of satellites around the fundamental reflections. Next the crystal was heated for 82 days at 270 °C in vacuum to give crystal 3b of Table 1. After annealing, the intensity of the reflection was measured again. The profiles of a few selected reflections are presented

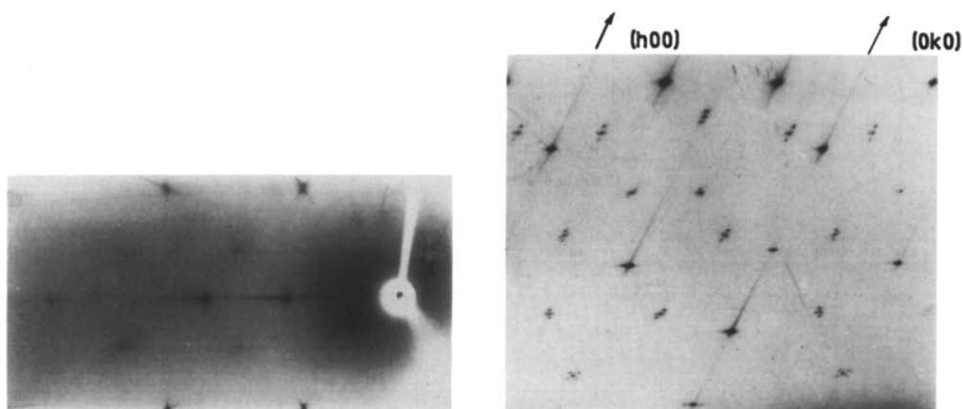


Fig. 1. X-ray rotation photograph of  $\text{Au}_{31.6}\text{Cu}_{68.4}$  crystal; rotation axis  $[110]$ .

Fig. 2.  $hk0$  X-ray Weissenberg photograph of  $\text{Au}_{31.6}\text{Cu}_{68.4}$  ( $\text{AuCu}_3^{\text{II}}$ ) crystal.

in Fig. 3. The halfwidth and intensity of the reflections for crystal 3b are larger than for crystal 3a.

### 2.1.3. Data from Bond diffractometer

The lattice parameter  $a$  for a subcell of crystal 4 was measured on the Bond diffractometer. During the measurements (8 h duration) the crystal remained in the evacuated and sealed quartz capillary. The results are presented in Fig. 4. A linear region above 630 K corresponding to the existence of the  $\alpha\text{-AuCu}_3$  phase and a linear region below 520 K apparently corresponding to the existence of the  $\text{AuCu}_3^{\text{I}}$  phase can be clearly identified. The intermediate region corresponds to the existence of the  $\text{AuCu}_3^{\text{II}}$  phase. We also observed that if we measured the cell parameter at a certain temperature below the  $\text{AuCu}_3^{\text{II}}$  region, we obtained a slightly lower value with increasing time.

### 2.1.4. Data from powder diffractometer

Powder specimens were annealed under conditions similar to those used for single crystals. Specimens annealed at 850 and 800 °C gave only the fundamental reflections, but that annealed at 800 °C showed a pronounced elevation of the background around the theoretical position of the (100) superlattice line. The specimen annealed at 340 °C showed superlattice lines with the (110) triplet characteristic of an LPS (Fig. 5(a)). After annealing for 8 weeks at 270 °C the superstructure lines became broader and the (110) triplet transformed into a rather irregular band (Fig. 5(b)). After annealing for another 26 weeks at 270 °C the normal (110) superstructure line was observed, but simultaneously a very weak new line consistent with the (111) line from  $\text{AuCu}^{\text{I}}$  was also observed (Fig. 5(c)). Subsequently the sample was annealed for a further 2 weeks at 200 °C but no change was observed.

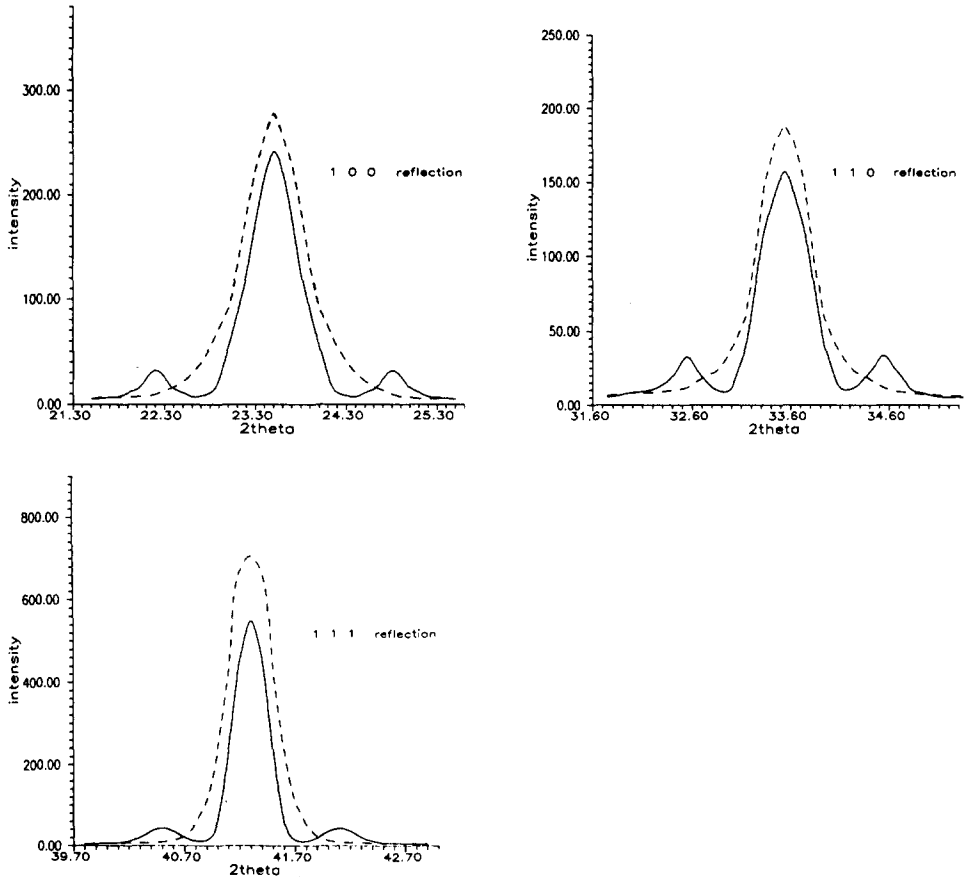


Fig. 3. Reflection profiles for  $\text{Au}_{31.6}\text{Cu}_{68.4}$  crystal (solid line before and dashed line after annealing at  $270^\circ\text{C}$ ).

## 2.2. $\text{Au}_{50}\text{Cu}_{50}$

As mentioned, data obtained from X-ray diffraction studies on AuCu crystals have already been published [1]. In this paper we present data from polycrystalline samples. First, we prepared a powder sample of  $\alpha$ -AuCu. Its powder diffraction pattern showed an f.c.c. cell. Next the sample was annealed at  $270^\circ\text{C}$ . After 1 day the cubic symmetry was still observed, although weak superstructure lines (001) and (110) were clearly visible (Fig. 6(a)). After 2 days the diagram showed tetragonal symmetry consisting of an  $\text{AuCu}^I$  superstructure ( $a = 3.972 \text{ \AA}$ ,  $c = 3.665 \text{ \AA}$ ) (Fig. 6(b)). After 30 days the diagram showed the same tetragonal phase but with a slightly bigger unit volume ( $a = 3.978 \text{ \AA}$ ,  $c = 3.682 \text{ \AA}$ ). Moreover, an additional weak line was observed. We believe that this must be the (111) line from essentially pure copper with a cell parameter of  $3.6312 \text{ \AA}$  (Fig. 6(c)).

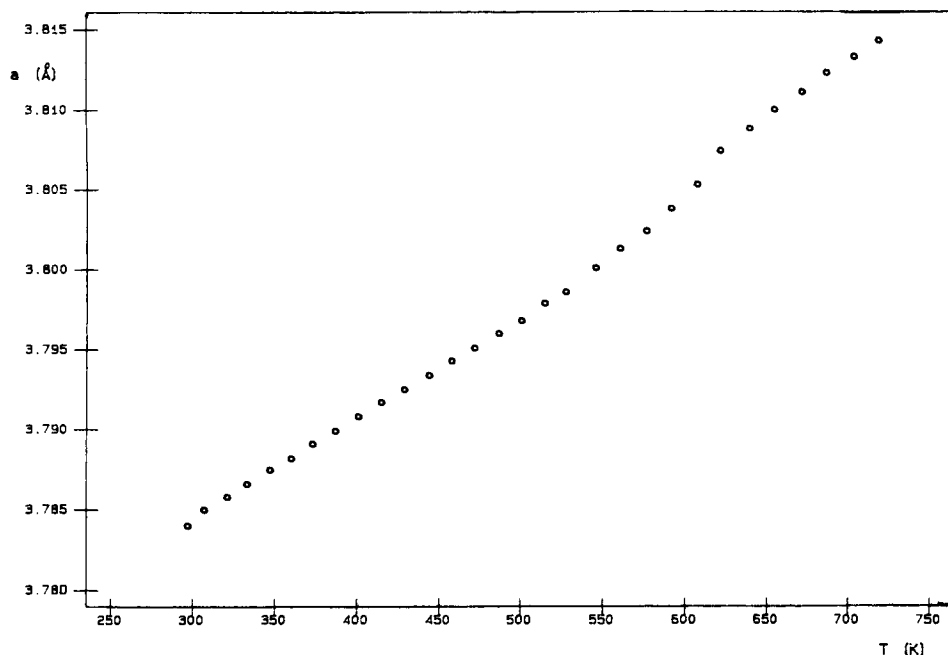


Fig. 4. Lattice parameter *vs.* temperature for crystal 4 from Bond diffractometer.

### 2.3 $Au_{75}Cu_{25}$

First the powder diagram of a disordered alloy was taken showing f.c.c. lines only. Next this sample was annealed for 26 weeks at 270 °C to give the powder diagram shown in Fig. 7. As can be seen from this figure, the observed  $AuCu^I$  phase has separated from the cubic matrix.

## 3. Discussion

X-ray photographs of the  $Au_{31.6}Cu_{68.4}$  crystals quenched from 850 and 800 °C indicate that at 850 °C a true solid solution is present, but already at 800 °C (Fig. 1) an appreciable short-range order exists. These correspond to the  $\alpha$  and  $\alpha^{II}$  states of ref. 10. For both single-crystal and powder samples of  $Au_{31.6}Cu_{68.4}$  annealed at 340 °C we found that our results are not in complete agreement with Scott's results [2]. In particular satellites are always observed together with the superstructure reflections and satellites are also present around the fundamental reflections (see Fig. 3), giving support to Williams' conclusion [11] that already in the LPS state the alloy is not entirely homogeneous. This is consistent with results obtained from samples annealed at 270 and 200 °C showing quite distinct inhomogeneity. In contrast to ref. 5, we could not find any indication of a cubic-to-tetragonal  $AuCu_3^{II}$  transformation, either from thermal expansion measurements (Fig. 4) or powder diffraction patterns (Fig. 5).

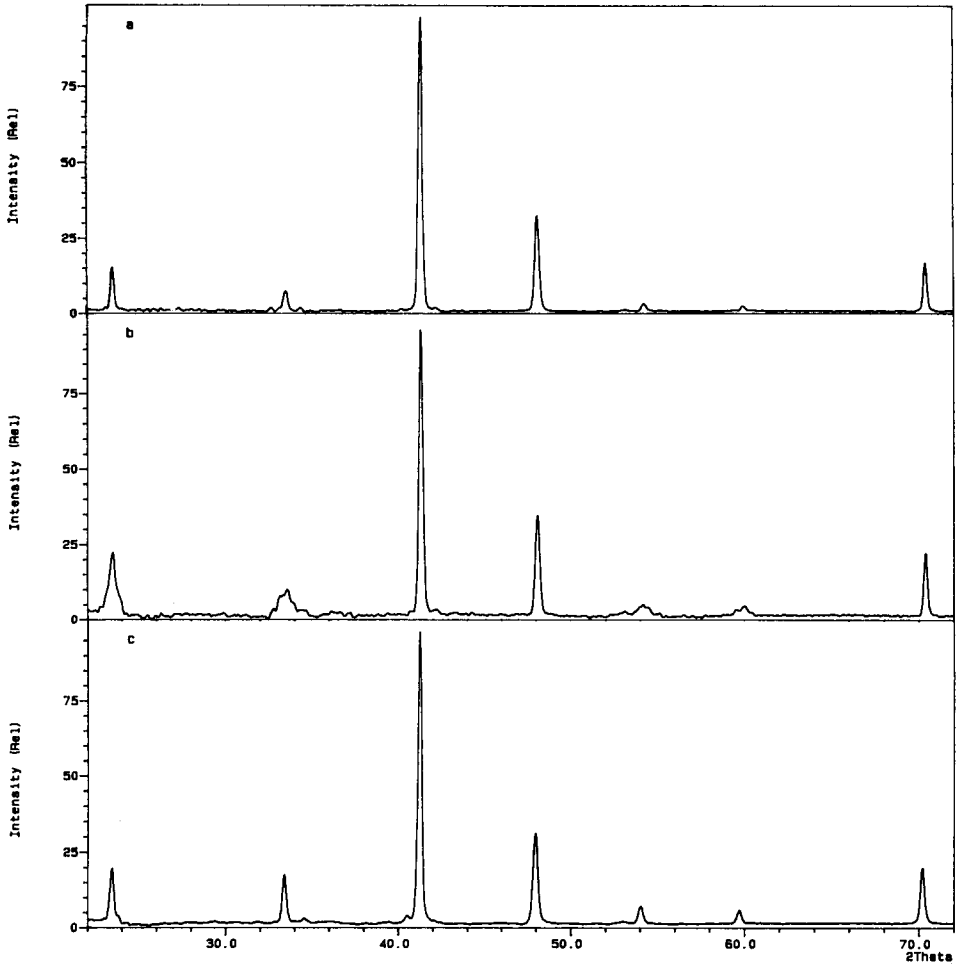


Fig. 5. X-ray powder diffraction diagrams of  $\text{Au}_{31.6}\text{Cu}_{68.4}$  alloy.

As the powder diffraction diagrams for AuCu show, even for this composition a degree of order exists which is sufficient to give observable superstructure lines, even though cubic symmetry may be preserved (Fig. 6). The tetragonal  $\text{AuCu}^{\text{I}}$  phase finally appears after some threshold value of the order has been reached (Figs. 6(a) and 6(b)). Further annealing leads to the appearance of a second phase, *i.e.*  $\text{Cu}(\text{Au})$ . We deduce that the X-ray diagrams for the ordered  $\text{Au}_3\text{Cu}$  in ref. 6 are also from inhomogeneous samples, because they are very similar to that presented in Fig. 5(b). Moreover, as was shown by us (Fig. 7), in the initially homogeneous alloy  $\text{Au}_{75}\text{Cu}_{25}$  after annealing at 270 °C the  $\text{AuCu}^{\text{I}}$  phase does appear. Tu and Berry [12] also observed that at 200 °C the  $\text{AuCu}^{\text{I}}$  phase grows at the expense of  $\text{Au}_3\text{Cu}$ . Therefore we think that generally in Au–Cu alloys with decreasing temperature there is an increasing tendency towards separation of the constituent atoms (but at a simultaneously decreasing rate). This is realized by different ordered

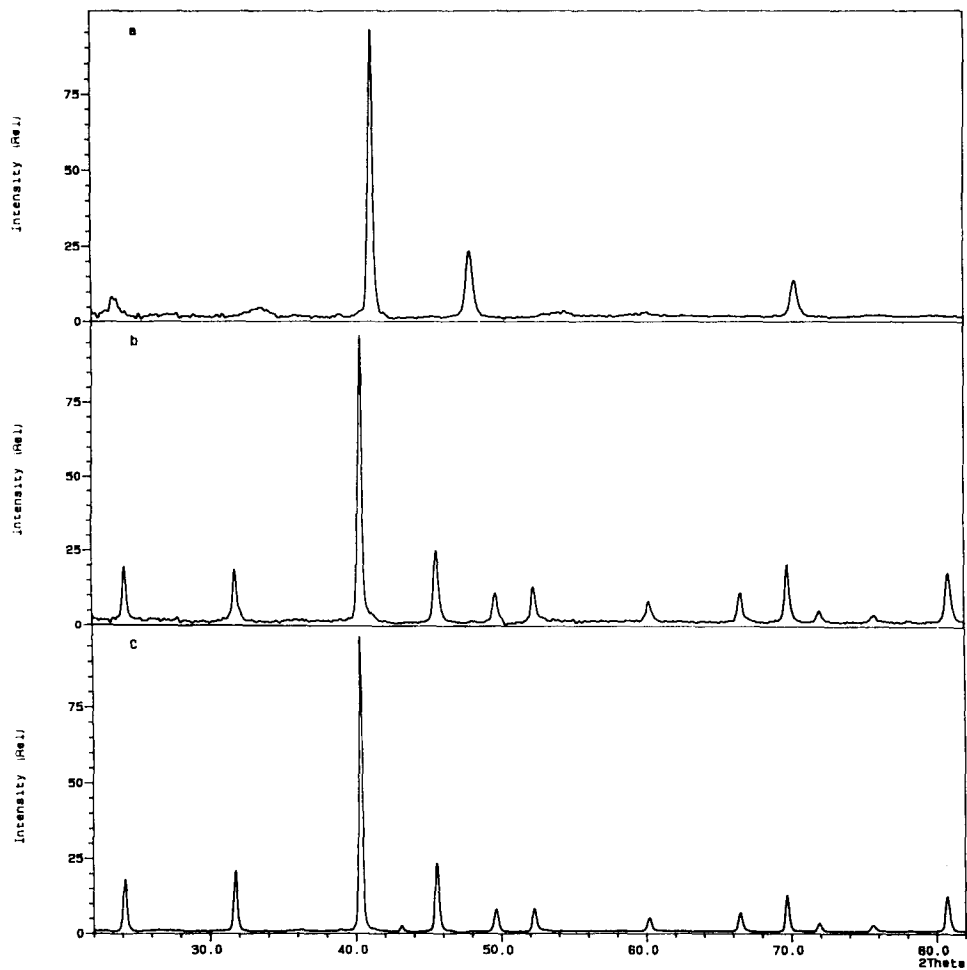


Fig. 6. X-ray powder diffraction diagrams of  $\text{Au}_{50}\text{Cu}_{50}$  alloy.

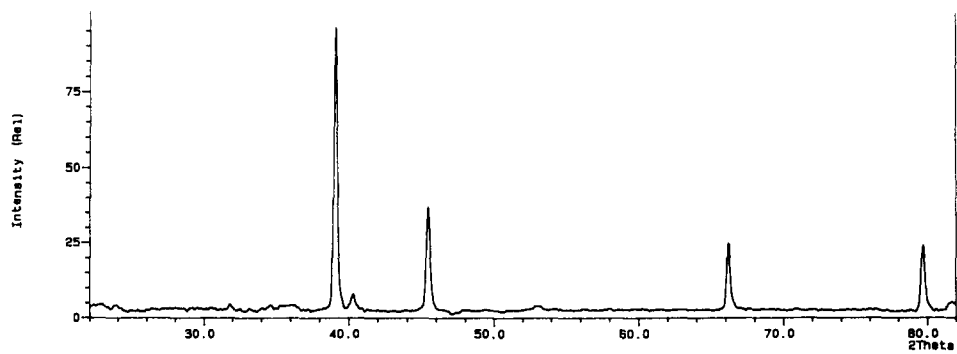


Fig. 7. X-ray diffraction diagram of  $\text{Au}_{75}\text{Cu}_{25}$  alloy after annealing for 26 weeks at 270 °C.

states and their degree of order beginning with short-range order, through LPS superstructures up to macroscopic phase separation. From this point of view it is obvious that the most stable ordered phase in the Au–Cu system is AuCu<sup>I</sup> (in this structure each (002) plane is a copper or gold plane).

As was shown in ref. 13 copper atoms are able to be transported via diffusion through the ordered layers and therefore it is very likely that annealing processes lead to some relative enrichment of the outer layers of the alloy with copper atoms. This is probably the main reason for the decrease in cell parameter with time as measured by X-ray diffraction. Moreover, temporary equilibrium could be easily changed as a result of oxidation of copper atoms on the surface. This might have been the case in the experiment of ref. 5. Although it does not appear possible to establish a true equilibrium, we are convinced that our X-ray results for Au<sub>31.6</sub>Cu<sub>68.4</sub> give substantial support to Williams' model of an LPS [11]. We suggest that in the case of AuCu<sup>II</sup> the complex LPS is realized also by peculiar microtwinning and alternation of the basic tetragonal cell, as was recently shown by us [1].

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