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Phase transitions in $Au_{0.5}Cu_{0.5}$

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Abstract. After having recalled the crystal structures of the three equilibrium phases of stoichiometric $Au_{0.5}Cu_{0.5}$ alloy, new results are presented in the frame of a general discussion on the transition series (with increasing temperature) :

AuCu I ($L1_0$) → AuCu II → disordered AuCu (A1).

Both transitions have been followed by in-situ temperature X-ray, confirming earlier electron diffraction studies, and their transition enthalpies have been measured by differential scanning calorimetry. These results are commented, and a possible explanation for the large two-phase hysteresis (35°C) is proposed.

1. THE THREE EQUILIBRIUM PHASES OF $Au_{0.5}Cu_{0.5}$

The equiatomic AuCu alloy can display three phases : the tetragonal (c/a=0.92) ordered $L1_0$ structure (AuCu I) at low temperature, the orthorhombic incommensurate structure AuCu II (first investigated through X-ray diffraction by Johansson and Linde [1]) from less (see below) than 385°C up to about 420°C, and the disordered fcc A1 structure at higher temperature.

The crystal structures of the $L1_0$ and A1 phases are well known :

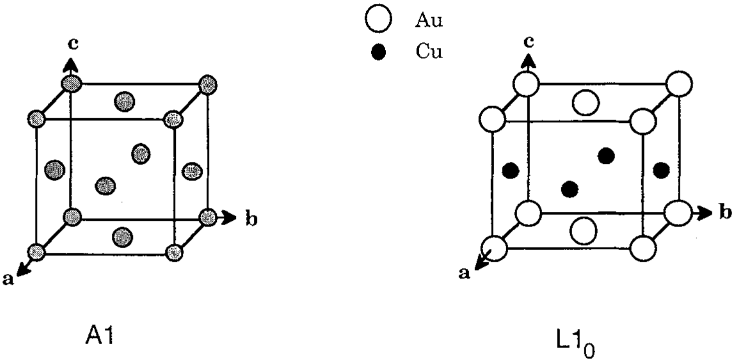

Figure 1. The cells of the A1 (disordered) and $L1_0$ (ordered) structures

The AuCu II cell drawn on the following figure is the Johansson-Linde cell (space group Imam).:

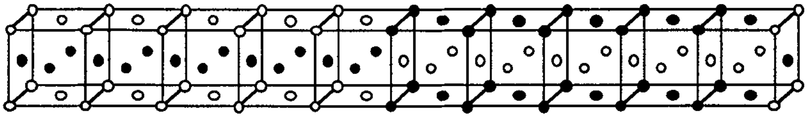

Figure 2. The periodic antiphased (PAP) structure (The orthorhombisation has been neglected)

There is juxtaposition of M=5 $L1_0$-units along **b**, then an antiphase boundary of shift vector $[\frac{1}{2}\,0\,\frac{1}{2}]$ operates, which is followed by M=5 shifted $L1_0$-units. After a 2Mb=10b spacing, the same shift vector intervenes and the cell is restored.

Table 1. Parameters of the three phases (measured at 20°C) [5]

$L1_0$ (annealed several days at 300°C and quenched)		PAP (annealed several days at 390°C and quenched)			A1 (quenched from 450°C)
a (Å)	c (Å)	a (Å)	b (Å) (≈ 10a)	c (Å)	a (Å)
3.960	3.670	3.962	39.74	3.659	3.874

After the discovery of this phase, numerous observations by electron microscopy followed (the first ones are reported in [2-4]), imaging (in dark field) the periodic antiphase boundaries. However, it was found later, through the study of X-ray diffraction intensities [5,6] and of high resolution electron microscopy [7,8], that the Johansson-Linde model is only approximate. Actually, these numbers (M) of $L1_0$-units are *randomly fluctuating around a mean value* $\overline{M}$. In fact, *there is no cell*, only an average. The antiphase boundaries are randomly wavy around a mean plane. The following figure shows an antiphase domain between two wavy boundaries.

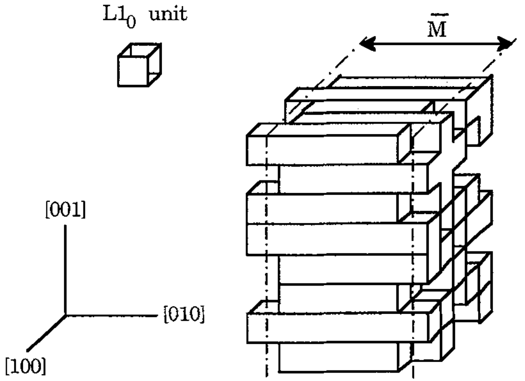

Figure 3. An antiphase domain between two wavy boundaries

AuCu II is thus a *statistical* periodic antiphased (PAP) structure, with a mean long period of 2 $\overline{M}$ b along the **b** axis. Besides, when the composition is changed, on both sides of 50 at.%, $\overline{M}$ varies *continuously*, taking all values (between 5 and 6.5) including incommensurate ones. Although basically ordered, this phase is only a semi-ordered structure since it accommodates some disorder located at the antiphase boundaries. This corresponds quite well to its intermediate *thermodynamic position in the transition series between an ordered* ($L1_0$) *and a disordered* (A1) structure. This located disorder persists unchanged, even after very long annealing, showing that the PAP structure is a true stable thermodynamic phase.

2. RESULTS OF IN-SITU X-RAY DIFFRACTION

In-situ observation of the onset of the PAP phase from $L1_0$, through both electron [9] and X-ray [10] diffraction, has shown the unexpected result that the PAP phase begins to appear at a temperature as low as 350°C after a sufficient annealing time, contrary to the onset temperature which is generally admitted (around 385°C [5]).

The diffraction lines 110 (characteristic of $L1_0$) and 1,9,0 and 1,11,0 (characteristic of PAP) have been recorded at various temperatures. The following figure explicitly shows the two successive transitions.

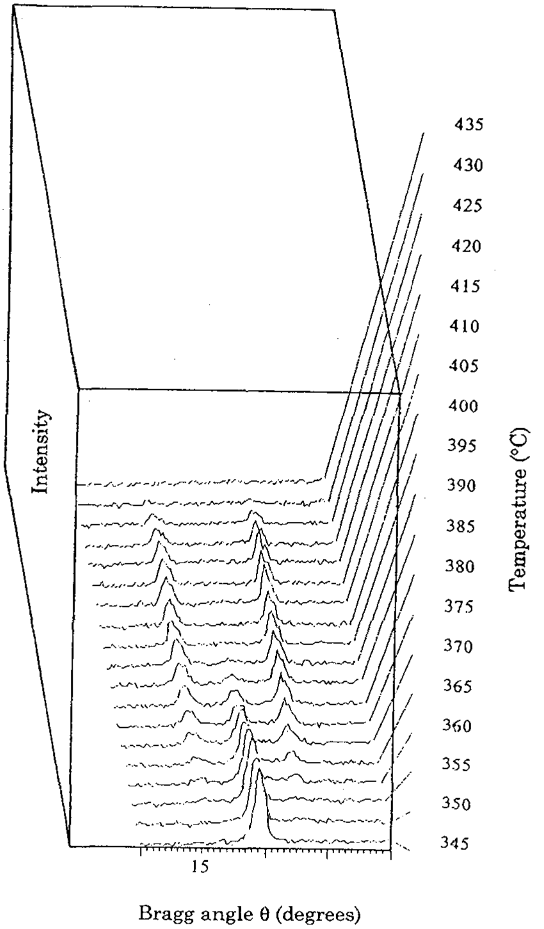

Figure 4. In-situ X-ray diffraction patterns (14 to 18°), showing the successive transitions

The low temperature of the onset of AuCu II is followed by a two-phase hysteresis of 35°C. The existence of this two-phase range has been confirmed by kinetic studies [10].

3. THERMODYNAMIC RESULTS

Working on samples (amounts between 200 and 300 mg) of well determined starting states the following results were obtained by differential scanning calorimetry (DSC) [10] (see Table 2).

On the following figure, the general aspect of the heat effect of the successive transitions is shown, stressing their very different features.

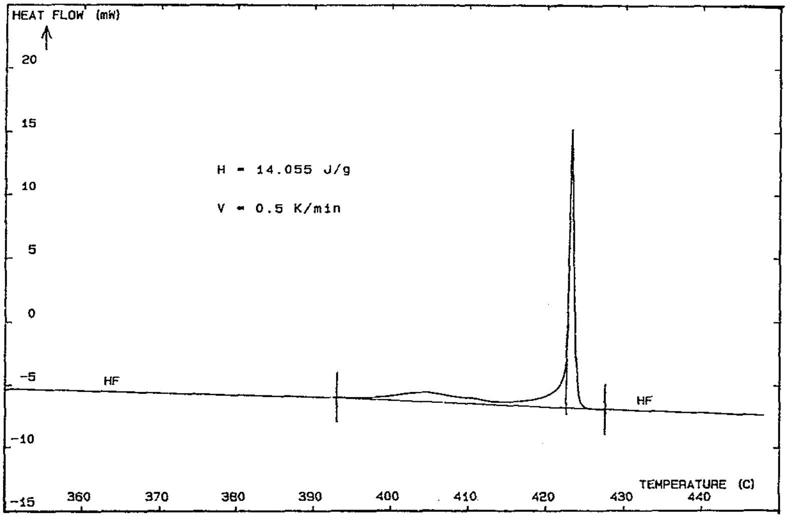

Figure 5. DSC curves showing the successive transitions

Table 2. Results of the DSC experiments (rate : 0.5 K/min) . The temperatures T_1 and T_2 are, respectively, the temperatures of the onset of the transitions $L1_0$ → PAP and PAP → A1.

T_1 (°C)	ΔH_1	T_2 (°C)	ΔH_2
397.5±1	2.5(±0.5) $J.g^{-1}$ =325.6(±65.1) $J.mol^{-1}$	422.1±0.5	9.4(±0.5) $J.g^{-1}$ =1224.4(±65.1) $J.mol^{-1}$

4. DISCUSSION

The onset temperatures obtained by DSC are higher than those observed in X-ray or electron diffraction. A natural explanation is that this is a kinetics effect : the rates 0.2 or 0.5 K/min would be too high compared with the nearly isotherm in-situ diffraction observations. However, more generally, although the onset of even a small atomic regularity is detectable by diffraction, it may well be associated with a very weak energy absorption, thus being undetectable by calorimetry.

Regarding the hysteresis of the AuCu I → AuCu II transition, the following explanation could be given. If, as is generally admitted, the composition is that of the congruent point, there is no change of composition when the nuclei of the new (II) phase forms, and thus we can reason as if it was the allotropic transformation of a pure substance. Interfacial free enthalpy must then be put into the free enthalpy balance to obtain the condition for the nuclei of the phase II to appear into the matrix (I). If ΔG is the total change of the free enthalpy of the system, it must cancel at the transition temperature (the pressure is fixed at one atmosphere). At any temperature T, we have :

$$\Delta G(T) = -\Delta G^{I}(T) + \Delta G^{II}(T) + \Delta G^{\Omega}(T)$$

where $\Delta G^{I}(T)=\mu^{I}(T)\Delta n^{I}$ is the free enthalpy of the part of the matrix (I) which has transformed into II; $\Delta G^{II}(T)=\mu^{II}(T)\Delta n^{II}$ is the free enthalpy of the new phase (II) issued from this latter part; and $\Delta G^{\Omega}(T)$ is the free enthalpy of the interface I/II created by the transformation; $\Delta G^{\Omega}(T)$ is essentially positive. Of course, $\Delta n^{I}=\Delta n^{II}$. We thus have :

$$\Delta G(T) = (\mu^{II}(T) - \mu^{I}(T))\Delta n^{II} + \Delta G^{\Omega}(T)$$

Let us denote T_0 the "ideal" temperature of the I→II transition, i.e. the transition temperature when interface effect is neglected. Here, when $T=T_0$, we have :

$$\Delta G(T_0) = (\mu^{II}(T_0) - \mu^{I}(T_0))\Delta n^{II} + \Delta G^{\Omega}(T_0)$$

By definition of T_0, we have $\mu^{II}(T_0) = \mu^{I}(T_0)$. So there remains :

$$\Delta G(T_0) = \Delta G^{\Omega}(T_0) > 0$$

This shows that the I→II transition cannot occur at T_0, but at a higher temperature. A first result of this analysis is therefore that the temperature of the onset of the I→II transition is delayed from T_0 to a higher value T_1. At $T=T_1$ we thus have :

$$\Delta G(T_1) = 0 = (\mu^{II}(T_1) - \mu^{I}(T_1))\Delta n^{II} + \Delta G^{\Omega}(T_1)$$

where now $\mu^{II}(T_1) < \mu^{I}(T_1)$. Therefore, T_1 is determined by the equation :

$$\mu^{II}(T_1) = \mu^{I}(T_1) - \frac{\Delta G^{\Omega}(T_1)}{\Delta n^{II}}$$

Now what happens when this temperature is maintained ? The formation of II proceeds, thus increasing Δn^{II} and also $\Delta G^{\Omega}(T_1)$. However, as soon as the value of the ratio $\frac{\Delta G^{\Omega}}{\Delta n^{II}}$ changes, the above equality is no more valid, and the formation of the new phase (II) stops. The temperature must then be increased in order that the I→II transformation resumes. And so on. We thus can see why there is a two-phase hysteresis of ΔT=35°C.

As to the order of the transitions, while AuCu II → disordered AuCu is clearly of the first order, there has been some uncertainty among authors about AuCu I → AuCu II. It is true that this latter transformation is very spread in temperature, in fact much more than was reported up to now; besides, the thermal effect is small. These two data might point to a second order transition. But there is a well defined peak in DSC, and two diffraction patterns clearly separated, indicating a two-phase state. This seems to show that this latter transition also is of the first order.

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