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Lattice Parameters of the CuAu(I) Phase

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Despite the many studies of Cu-Au alloys, it seems that the lattice dimensions of the CuAu(I) phase have never been measured continuously as a function of composition. The composition dependence of these parameters is of interest, however, since a change in the slope of a and c *versus* composition at $\sim$ 50 atomic % is expected on the basis of the corresponding data for the isostructural phases in the Ir-Mn, Ni-Mn, Pd-Mn, and Pt-Mn systems.[1-4]

The ordering in the CuAu(I) type structure establishes alternate layers of Cu and Au atoms normal to the unique axis, and atomic contacts within the layers occur along [100] and [010] of the primitive cell containing two atoms. The filling of one layer with the larger Au atoms as the Au content of the phase increases towards 50 atomic %, must accordingly cause the a parameter to increase. When the Au layer is filled at 50 atomic %, we expect the a spacing to be about equal to the atomic diameter of pure Au. Beyond 50 atomic % Au, when Au starts to enter the Cu layer, interlayer Cu-Au contacts are replaced by Au-Au contacts, causing the c parameter to expand (since a has already expanded to accommodate the Au-Au contacts). These compulsory expansions of a below 50 atomic % Au and of c above 50 atomic % Au control the dimensions of the unit cell, and the variations of c below and of a above 50 atomic % Au only keep the appropriate volume for the unit cell. These conditions must cause a change of slope in the lattice parameter curves at the equiatomic composition.

Experimental. Alloys ranging from 40 to 60 atomic % Au at intervals of 2 atomic % were prepared by melting weighed quantities of 99.99 + % pure Cu and Au in evacuated, sealed silica (clear) tubes. The alloys were annealed for 6 h at 650°C (to reduce the number of nuclei for ordering and hence to increase the ordering rate [5]) and then annealed at 300—310°C for more than 16 months, with intermittent cold work treatments, including the preparation of filings and X-ray examination. Nominal compositions were considered sufficiently accurate.

X-Ray powder photographs were taken with Cu$K\alpha$-radiation in a 190 mm diameter Unicam camera. The lattice constants were determined from the high-angle reflections by a Nelson-Riley [6] type extrapolation. Guinier photographic data of all alloys were collected with a 80 mm diameter camera using monochromatized Cu$K\alpha_1$-radiation (λ = 1.54050 Å) and KCl as internal standard. The lattice constants calculated from the latter data were refined by applying the method of least squares. Unit cell dimensions determined by these two methods agreed within $\pm$0.001 Å.

Results. The CuAu(I) phase appears to have a homogeneity range between 46 and 54 atomic % Au for alloys annealed at $\sim$ 300°C. Alloys from 40 to 44 and from 56 to 60 atomic % Au contained the CuAu(II) phase or mixtures of phases (CuAu(I), CuAu(II), and $CuAu_3$), in fair agreement with the data given in Hansen[7,8] and/or Pearson.[9,10]

The measured lattice parameters of the CuAu(I) phase (Fig. 1) do indeed show the predicted change in slope at 50 atomic % Au, but this is not apparent in the unit

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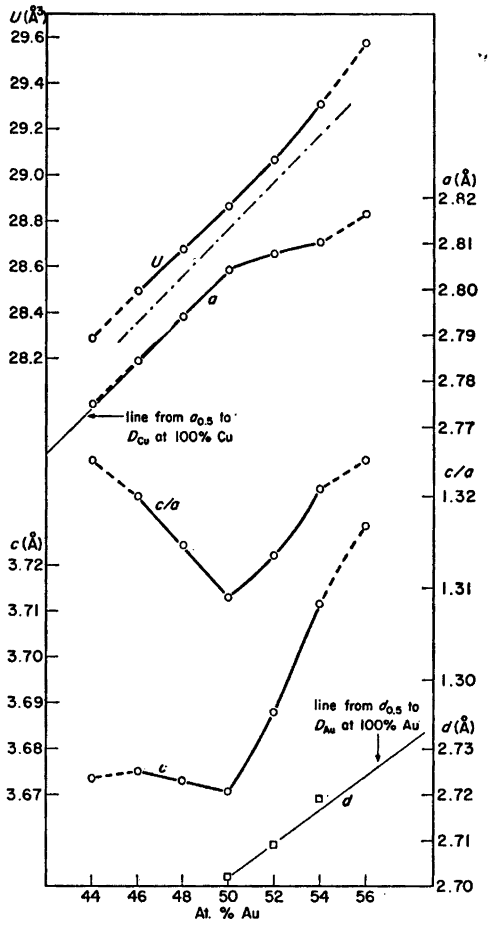

Fig. 1. Lattice parameters (a, c, and c/a), unit cell volume (U), and interlayer interatomic distance (d) of the CuAu(I) phase as a function of composition.

Full line ——— indicates homogeneous CuAu(I) phase.

Broken line – – – to alloys at 44 and 56 atomic % Au indicates variation of the CuAu(I) pseudo-cell parameters for alloys in the CuAu(II) or two-phase fields.

Chain line —·—·— gives the line joining twice the atomic volume of Cu at 0 atomic % Au to twice the atomic volume of Au at 100 atomic % Au.

The significance of the thin lines for a and for d is indicated on the diagram.

cell volume which runs very close to a line joining the doubled atomic volumes of Cu and Au, being about 0.33 % above it at the equiatomic composition.

If the changes in the lattice parameters do result from size effects as suggested in the introduction, we would expect the value of the a parameter at Au-poor compositions to depend on the fraction of Au-Au contacts in the Au layer, so the a spacing should lie on a line joining the atomic diameter of Cu (D_{Cu}) at 0 atomic % Au (no Au-Au contacts) to the value of a at 50 atomic % Au (all Au-Au contacts in the layer). Secondly, since the interlayer interatomic distance, d, at 50 atomic % Au represents all Cu-Au contacts, and at 100 atomic % Au it would represent all Au-Au contacts, the d values in the Au-rich region should lie on a line joining the value of d at 50 atomic % to the diameter of pure Au (D_{Au}) at 100 atomic % Au. These expectations are fairly well borne out in Fig. 1 confirming that the lattice parameter variations and changes of slope at the equiatomic composition result only from size effects, and that there is no indication of strong A-B type interactions. The closeness of the atomic volume of the CuAu(I) phase to that predicted from the atomic volumes of the two components, is also consistent with these observations, supporting the idea that ordering at atomic ratios of 3:1 and 1:1 in simple metallic phases, such as the Cu_3Au, Ni_3Sn, and CuAu(I) types of structures, results mainly from size effects.

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Studies on Plasminogen Activators

IV. An Enzyme Complex with Esterase Activity in Streptokinase-activated Human Plasma

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In previous work it was demonstrated that streptokinase (SK) interacts with normal as well as fibrinogen-free human plasma proteins causing the formation of an enzymatically active complex, which could be separated by gel filtration.[1,2] The molecular size corresponded approximately to the 19 S proteins as shown by sucrose density gradient ultracentrifugation. Recent work [3] demonstrates that the enzyme complex displays esterase activity on α-N-acetyl-L-lysine methyl ester (ALMe), while having no proteolytic effect on fibrin. This indicated that the complex formation may involve a protein binding of a similar type as recently demonstrated with trypsin.[4,5] Mehl *et al.*[5] suggested that the human α_2-macroglobulin may function as the binding protein, reporting a sedimentation constant of 19.8 S. In earlier studies Haverback *et al.*[4] showed that 15—20 S protein in human plasma combines with trypsin and chymotrypsin yielding an enzyme with esterase action but no longer inhibited by soybean. Our results are in agreement with these findings, since the protein complex isolated after incubation of human plasma with SK had esterase action on ALMe, however, was not inhibited by soybean, nor by low concentrations of ε-aminocaprocic acid (ε-ACA).[3] When the concentration of ε-ACA was increased to 0.3 to 0.6 M inhibition occurred. The esterase activity was between 3.3 to 5.4 μmoles of ALMe hydrolyzed per hour per mg measured with the protein complex isolated after gel filtration.[3]

Lanchantin *et al.*[7] recently presented evidence for the binding of human thrombin to the trypsin-binding macroglobulin, suggesting that this kind of complex formation occurs with the esterase-type of proteolytic enzymes. As pointed out by Wilding *et al.*[8] α_2-macroglobulin has an established position as a carrier in the transport of several substances in serum. While the reactions leading to the SK-induced fibrinolytic activation in human plasma are yet not known in detail, it seems evident that once activated, plasmin should form a similar complex. Recent work by Ganrot [9] reports that plasmin binds to α_2-macroglobulin, blocking about half of its trypsin binding capacity, which suggests a higher affinity of this protein for trypsin. Recent results revealed that the SK-esterase complex [3] may be dissociated in two protein peaks with esterase activity by ultracentrifugation at pH 7.8 against a sucrose gradient. Compared with standard albumin the component with the slower sedimentation rate behaved as a 7 S protein with an approximate molecular weight comparable to plasmin. However, a proteolytic response could not be shown with the corresponding protein fractions on heated fibrin plates. A proteolytic effect was observed, however, by the decrease in the total protein content during prolonged dialysis of the SK-esterase complex at pH 7.8 and +5°C. This effect was time dependent and could be avoided by lowering the pH to 6.[3] Similarly no dissociation occurred when ultracentrifugation of the enzyme complex was performed at pH 5.3. Previous experiments had shown that the esterase complex was filtered through the Sephadex G-200 gel as a homogeneous peak over the pH range from 8 to 5.5, as concerns the plasminogen activating effect on bovine fibrin plates.

In order to avoid the overlapping by 7 S material after gel filtration [1,2] the SK-esterase complex used for the ultracentrifugation experiment shown in Fig. 1 was a recycled preparation corresponding only to half the active peak filtered immediately following V_0. The apparently homogeneous complex obtained by gel filtration[1-3] over the pH range mentioned above, dissociated in two active components at pH 7.8 after