8.3-2   X-RAY, ELECTRON DIFFRACTION AND HREM INVESTIGATIONS OF THE METASTABLE COMPOUND $Au_4Si(m)$ <u>M. Ellner</u>, E. Lukačević, W. Mader and K. Schubert, Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaften, Seestr. 75, D-7000 Stuttgart 1, FRG

Gold and silicon are almost completely immiscible in the solid state. They form a simple eutectic at about T = 636 K and x_{Si} = 0.186. The first amorphous alloy produced by use of splat-cooling technique was found in this system, at x_{Si} = 0.25 (Klement, Willens & Duwez, Nature, 1960, <u>187</u>, 869). Metastable crystalline compounds can be obtained either by annealing of amorphous alloys, or by quenching of liquid alloys at lower quenching rates. Two different X-ray powder diffraction diagrams were found for alloys quenched from the melt: the first one corresponding to alloys with x_{Si} < 0.25 and the second one corresponding to alloys with x_{Si} > 0.25 (Suryanarayana & Anantharaman, Mat. Sci. Eng., 1974, <u>13</u>, 73).

For the silicon-poor metastable compound, a homogeneity at about Au_4Si was established. Guinier powder diffraction photographs with $CuK\alpha_1$ and $MoK\alpha$ radiation displayed strong and weak lines, characteristic for the presence of a superstructure. The indexing of the strong diffraction lines yielded a substructure unit cell based on the body centred cubic Bravais lattice (B) with a = 5.554(1) Å (Ellner & Predel, Z. Metallkd., 1980, <u>71</u>, 364). The macroscopic density (d_m = 15.9$_2$ Mgm^{-3}) and the lattice parameter gave 10 atoms in the substructure unit cell (cI10). Metallographic sections showed small grains as in the splatted alloys not suitable for the single crystal X-ray diffraction. Therefore, selected area and high-resolution electron microscopy were used to determine the superstructure cell. In order to obtain sharp diffraction spots, the splat-cooled samples were annealed 16 h at 375 K. The electron diffraction patterns $(h0l)_B$ and $(hkh)_B$ displayed an orthorhombic superlattice Q, related to the substructure B such that: $(a_Q,b_Q,c_Q) = (a_B,b_B,c_B)$ (3,0,1; 0,1,0; 3,0,-1) = 23.633(6); 5.543(2); 7.872(2) Å. The refinement of the lattice parameters was made by use of Guinier photographs ($CuK\alpha_1$, Si internal standard). The condition "$(hkl)_Q$ only with h+k=2n" for possible reflections was confirmed in the electron diffraction patterns $(h0l)_Q$ and $(0kl)_Q$; an additional condition "$(hk0)_Q$ only with h=2n and k=2n" was observed in Guinier photographs and in the $(hk0)_Q$ electron diffraction patterns and the condition "$(0kl)_Q$ only with k=2n and l=2n" was observed in the Guinier photographs and in the $(0kl)_Q$ electron diffraction patterns. These conditions for possible reflections are characteristic of the space group Ccmb and Cc2a.

08.3-3   PREPARATION AND STRUCTURAL INVESTIGATIONS OF Mn_3As_2 AND Mn_5As_4. By <u>M. H. Möller</u>, L. H. Dietrich and W. Jeitschko, Anorganisch-Chemisches Institut der Universität, Wilhelm-Klemm-Straße 8, D-4400 Münster, FRG.

Two modifications of Mn_3As_2 with unknown crystal structures were reported in the binary system manganese-arsenic (Gmelin Handbook of Inorganic Chemistry, 8th Edit., Vol. <u>56</u>, <u>C9</u>, 1983). Annealing powders of the elemental components in silica tubes at 760 °C for several days and cooling down to room temperature with various cooling rates gave well crystallized samples containing the high(β)- and/or low(α)-temperature forms of Mn_3As_2 often accompanied by the additional compound Mn_5As_4. The compound β-Mn_3As_2 melts incongruently and crystallizes in the monoclinic space group C2/m with a = 13.88(1) Å, b = 3.785(2) Å, c = 16.21(2) Å, β = 126.8(1)°, V = 681.9 Å^3, and Z = 8 formula units per cell. Most of the crystals are twinned, thus wrongly suggesting a face centered orthorhombic cell with lattice constants a = 13.88 Å, b = 3.785 Å, c = 129.8 Å, V = 6819 Å^3. The structure determination of β-Mn_3As_2 from single-crystal X-ray data resulted in a residual of R = 0.041 (64 variable parameters and 1551 structure factors). The As environments of the seven independent Mn atoms vary from tetrahedral over square pyramidal and trigonal bipyramidal to octahedral, augmented by additional Mn atoms. The four different As atoms are surrounded trigonal prismatically by Mn atoms with one or two more Mn neighbors outside the rectangular faces of the prisms. The resulting "effective coordination numbers" ECoN (R. Hoppe, Z. Kristallogr. <u>150</u> (1979), 23) vary from 7.4 to 8.7 for Mn and from 6.8 to 7.9 for As. β-Mn_3As_2 is a metallic conductor and shows no transition to a superconducting state above 2 K.

The structures of α-Mn_3As_2 and Mn_5As_4 were solved from "single-crystal" data of one intergrown specimen of the two phases. α-Mn_3As_2 crystallizes in the orthorhombic space group $Cmc2_1$ with a = 3.762 Å, b = 13.76 Å, c = 13.19 Å, V = 682.8 Å^3, and Z = 8. The final residual is R = 0.08 (30 variables, 1053 F's). Mn_5As_4 also has the space group $Cmc2_1$ and similar lattice constants: a = 3.762 Å, b = 13.76 Å, c = 12.13 Å, V = 627.9 Å^3. There are 4 formula units per cell and the structure was refined to R = 0.12 (27 variables, 1051 F's). Both structures are closely related to the β-Mn_3As_2 structure: α-Mn_3As_2 may be described as a shift variant of the β-form, while in Mn_5As_4 one of the Mn-positions of α-Mn_3As_2 is not occupied. The atoms surrounding the void position are shifted towards the center of the void and thus no hole remains.