MS26-O5 Incommensurately modulated crystal structures of Cu_3Si

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The phase diagram of Cu-Si [1-3] has three polymorphs for Cu_3Si: η'' at room temperature, η' and η at high temperature. Several models of crystal structure for these phases were proposed [4-6]. However, there are still considerable uncertainties on the structure of these phases, and especially the crystal structures of η'' and η remain essentially unknown. We have undertaken a systematic study of bulk samples with varying composition to elucidate the complex phase diagram and definitely resolve the ambiguities in the structural description of all phases in the diagram. Samples with composition $Cu_{77}Si_{23}$, $Cu_{76}Si_{24}$ and $Cu_{75}Si_{25}$ were prepared by arc-melting and were measured by single crystal and powder X-ray diffraction. The average structure found is the same for the three compositions: $P6_3/mmc$, a=4.06 Å, c =14.66 Å. The structures at room temperature have two dimensional incommensurate modulations, with modulation vectors $\mathbf{q}_1$=(α,β,1/3) and $\mathbf{q}_2$=(-α-β, α,1/3). However, while the samples with composition $Cu_{77}Si_{23}$ yields diffraction pattern with α=β =0.251 and point group , both $Cu_{75}Si_{25}$ and $Cu_{76}Si_{24}$ have point group , with the direction of the modulation vectors shifted away from the diagonal with α=0.280 and β=0.206. The structure of the former phase is different from the previously reported structure of η'-Cu_3Si [6] in a doubled c lattice parameter and a different distribution of Cu and Si in the structure. The structure of the latter phase was observed for the first time, and differs from the phase with higher symmetry only in the arrangement of the modulated layers. Thermal analysis performed on the $Cu_{76}Si_{24}$ sample showed additional phase transition, reported in the literature previously [5,7], but not reported in the published phase diagrams. Diffraction experiments at high temperature are currently in progress.

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