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On the order in the hexagonal ζ -phase in the system silver-aluminum*

Massalski and Cockayne⁽¹⁾ have remeasured the lattice parameters in the system silver-aluminum and interpreted their results in the hexagonal ζ -phase by Brillouin-zone effects. They assumed a random solution, although thermodynamic^(2,3) as well as X-ray data^(4,5,6) indicate the existence of short range order in the silver-rich f.c.c α -phase and of clustering in the aluminum-rich f.c.c δ -phase.

The change of the lattice parameter in the ζ -phase could however also be explained in terms of an ordering in this phase.

While silver influences the lattice parameter of the δ -phase very little,^(1,7) the addition of aluminum to the α -phase causes a linear decrease of the nearest neighbor distance by 0.00085 Å/at. % Al. This same decrease is observed also in the hexagonal phase, considering the mean nearest neighbor distance. With increasing aluminum-content, however, the distance between nearest neighbors in the basal plane increases, while the distance between nearest neighbors in adjacent basal planes decreases. (See Table 1.)

TABLE 1. Nearest neighbor distances in the system Ag-Al, taken from Massalski and Cockayne⁽¹⁾

Composition	Phase	$d(\text{Å})$	$d'(\text{Å})$	$\bar{d}(\text{Å})$	$d''(\text{Å})$
Ag	α	2.889	2.889		
Ag-20 at. % Al		2.872	2.872		
Ag-25 at. % Al	ζ	2.870	2.865	2.868	2.865
Ag-33 at. % Al		2.878	2.844	2.861	2.861
Ag-40 at. % Al		2.885	2.831	2.858	2.855
Ag-80 at. % Al	δ	2.864	2.864		
Al		2.863	2.863		

- d : Nearest neighbor distance within close packed planes
- d' : Nearest neighbor distance between adjacent close packed planes
- \bar{d} : Mean nearest neighbor distance
- d'' : Nearest neighbor distance extrapolated from α -phase

Conversely assuming that one can draw conclusions from the interatomic distance as to the aluminum concentration, the following picture might apply: At 25 at. % Al there is very little difference between

alternate layers, but with increasing aluminum content a separation into Ag-rich and Al-rich layers occurs; at 40 at. % Al (the Al-rich phase boundary) one layer is almost pure silver (95 % Ag, 5 % Al), the other has a composition of 75 at. % Al and 25 at. % Ag. (See Table 2.)

TABLE 2. Composition of the ζ -phase (at. % Al)

Nominal composition	1st layer	2nd layer	Average composition
	2.889- d	2.889- d'	
	0.00085	0.00085	
25	22	28	25
33	13	53	33
40	5	(68)	(37)

That a layer structure like this might exist, is substantiated by work of Nicholson and Nutting,⁽⁸⁾ who found (001) superlattice reflections in particles precipitated from the δ -phase, although Westgren and Bradley⁽⁷⁾ did not detect these lines in the hexagonal phase. In agreement however with Nicholson and Nutting are Guinier⁽⁹⁾ and Ziegler⁽¹⁰⁾, who reported the existence of silver-rich platelets precipitating out on the (111) planes of the δ -phase. The sharp decrease of the heat of formation at the aluminum-rich boundary of the ζ -phase⁽³⁾ would also find its explanation in the decreasing number of Ag-Al bonds.

Work is in progress at Berkeley to determine from diffuse X-ray scattering of single crystals the degree of short range order in an alloy containing 33 at. % aluminum.

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