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The θ′ structure in aluminium copper alloys.

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The structure of the intermediate precipitate θ′, which is generally assumed to be of composition $CuAl_2$, was shown by Preston (1938) to be a distorted CaF_2-type structure, the cell being tetragonal. The unit cell has parameters $a = 4{\cdot}04$, $c = 5{\cdot}8$ Å and atomic positions:

Al in $0,0,0$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$; $0,0,\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},0$; and Cu in $\frac{1}{2},0,\frac{1}{4}$; $0,\frac{1}{2},\frac{3}{4}$.

(See Silcock, Heal & Hardy (1953–4, Fig. 19).)

It can be seen that the structure consists of alternate aluminium and copper layers but, in order to make all the layers close packed, two positions must be added to the copper layers. These are $0, \frac{1}{2}, \frac{1}{4}$ and $\frac{1}{2}, 0, \frac{3}{4}$ and are referred to later as the unoccupied sites.

The diffracting planes fall into three types:

Type 1: $2h+l = 4n\pm2$, $F^2 = (f_{Cu}-2f_{Al})^2$.
Type 2: $2h+l = 4n$, $F^2 = (f_{Cu}+2f_{Al})^2$.
Type 3: $2h+l = 2n+1$, $F^2 = (f_{Cu})^2$.

Guinier (1942) reported that the intensities of Type 1 reflexions were much higher than the calculated values. This has been confirmed, and the observed intensities, corrected as described below, are given in Table 1. The values obtained using Preston's structure are given in column (*A*).

The intensity values were obtained from single crystals, using focused monochromatic Mo $K\alpha$ radiation; the size of the beam at the specimen was approximately $2\frac{1}{2}$ mm. $\times$ 1 mm.

The integrated intensities obtained from sheet and rod specimens were corrected for absorption, geometrical factors and temperature. The average values, expressed as a ratio of the figure in italics, are given in Table 1.

Alteration of the percentage of copper atoms and distortions of the atomic positions did not give calculated values in agreement with observed intensities. It was necessary to postulate vacant atomic sites. All alterations proposed must occur at random in order that no new diffractions be introduced.

From Table 1 it can be seen that values obtained by assuming vacant aluminium sites (column (*B*)) are only slightly improved by exchanging copper for aluminium atoms in order to return the composition to $CuAl_2$ (column (*C*)). Vacancies in copper sites must be accompanied by exchange of aluminium for copper atoms in one pair only of the aluminium sites (i.e. 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ or $\frac{1}{2}, \frac{1}{2}$, 0 and 0, 0, $\frac{1}{2}$). This is improbable and, although the average agreement is better, the intensities of Type 3 planes are consistently low (column (*D*)).

The only way a good fit between observed and calculated values could be obtained was by assuming that atoms could be added to 'unoccupied' sites. This modification alone (column (*E*)) gives differences from the experimental values in the opposite sense to those from aluminium vacancies (column (*B*)) and the combination of the two modifications (columns (*F*) and (*G*)) gives the required F^2 values.

Table 1. *Intensities of θ′ reflexions*

Plane *hkl*	Type	F_o^2*	F_c^2 (*A*)	(*B*)	(*C*)	(*D*)	(*E*)	(*F*)	(*G*)
002	1	0·08	0·015	0·096	0·060	0·07	0·061	0·073	0·11
103	3	0·28	0·35	0·44	0·41	0·20	0·17	0·28	0·26
202	1	0·06	0·006	0·05	0·031	0·045	0·032	0·04	0·05
004	2	*1·0*	*1·0*	*1·0*	*1·0*	*1·0*	*1·0*	*1·0*	*1·0*
310	1	0·04	0·005	0·041	0·025	0·033	0·026	0·032	0·05
301	3	0·19	0·25	0·32	0·30	0·14	0·13	0·20	0·19
204	2	0·78	0·76	0·76	0·76	0·75	0·75	0·75	0·75
105	3	0·18	0·21	0·27	0·25	0·12	0·11	0·17	0·16
303	3	0·17	0·21	0·26	0·25	0·12	0·11	0·17	0·16
116	2	0·42	0·51	0·53	0·53	0·54	0·52	0·52	0·52
305	3	0·09	0·15	0·20	0·18	0·09	0·08	0·12	0·11
404	2	0·43	0·43	0·44	0·44	0·44	0·43	0·43	0·43
107	3	0·09	0·13	0·17	0·16	0·08	0·07	0·11	0·11
501	3	0·13	0·13	0·17	0·16	0·08	0·07	0·11	0·11
512	2	0·32	0·36	0·37	0·36	0·36	0·36	0·36	0·36
R†	—	—	0·31	0·41	0·37	0·19	0·24	0·12	0·12

* Average experimental values.
† $R = \Sigma\{(F_o-F_c)/F_o\}/13$, omitting 004 and 404.

(*A*) Preston's structure.
(*B*) Vacancies in aluminium sites. One atom in four missing.
(*C*) One in four aluminium sites vacant. One in six of the copper atoms replaced by aluminium.
(*D*) One in three of the copper sites vacant, one in four of one pair of aluminium sites replaced by copper.
(*E*) Every other unoccupied site ($0, \frac{1}{2}, \frac{1}{4}$; $\frac{1}{2}, 0, \frac{3}{4}$) filled with aluminium.
(*F*) One in eight of the aluminium sites vacant and one in four of the unoccupied sites filled with aluminium.
(*G*) One in six of the aluminium sites vacant and one in three of the unoccupied sites filled with aluminium.

Column (*F*) is probably the best fit obtainable, since it gives better agreement with the low-angle spots for which the intensity measurements are more reliable. This corresponds to removing one in eight aluminium atoms at random from an aluminium site and placing it at random on an 'unoccupied' site. The atoms in 'unoccupied' sites may, of course, be copper atoms. If entirely copper atoms the composition would be Cu_9Al_{14}, which is unlikely.

The relative increase in intensity of one type of reflexion from the θ′ structure may therefore be due to the removal of approximately one in eight aluminium atoms from an aluminium site and the insertion of these aluminium atoms in copper layers in positions not normally occupied. The positions of removal and insertion must be randomly distributed throughout θ′ and yet the average number must be constant.

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