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The Structure of $FeCu_2Al_7$ and T(CoCuAl)

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A ternary alloy in the CoCuAl system has been shown to be isomorphous with $FeCu_2Al_7$. Both structures have been accurately refined and a comparison of interatomic distances has been made. The suggestion that these are electron compounds could not be substantiated, as the only prominent Brillouin zone is considerably overlapped in both cases.

1. Introduction

In an examination of the Fe–Cu–Al system by X-ray powder methods Bradley & Goldschmidt (1939) found four ternary phases, of which the one entering into equilibrium with the Al-rich solid solution had the formula $FeCu_2Al_7$. Other workers have confirmed the existence of this phase, and although agreement has not been reached on the limits of the phase field, it is thought to be quite small.

The crystal structure of $FeCu_2Al_7$ was determined by Westgren, and is given (without details of accuracy) in an appendix to a paper by Phragmen (1950). The unit cell is tetragonal, with $a = 6{\cdot}33$, $c = 14{\cdot}81$ Å. Four units of $FeCu_2Al_7$ are placed in space group $P4/mnc$ as follows:

4 Al	in	4(*e*)	$(0, 0, z_1)$ etc.	*C*
4 Fe	in	4(*e*)	$(0, 0, z_2)$ etc.	*H*
8 Cu	in	8(*h*)	$(x_3, y_3, 0)$ etc.	*A*, *B*
8 Al	in	8(*g*)	$(x_4, \frac{1}{2}+x_4, \frac{1}{4})$ etc.	*F*, *G*
16 Al	in	16(*i*)	(x_5, y_5, z_5) etc.	*D*, *E*

(The capital letters refer to the atomic peaks of the (010) Fourier projection, Fig. 2.)

Westgren's parameters are given in Table 1. The structure may be described in terms of slabs and layers parallel to (001). The slabs consist of cubes of Al atoms, centred by Cu atoms, but with every fifth centre point unoccupied. Alternate slabs are displaced and rotated about the *z* axis. Between the slabs are flat layers of Al atoms in a square-and-triangle pattern (the *A*-layer of Black, 1956). The Fe atoms are placed alternately just above and below the squares of the *A*-layer, and are coordinated by 9 Al atoms. The ninefold polyhedron around the Fe atom has a square base, at the waist another larger square rotated with respect to the base, and a point at the top. This polyhedron is substantially the same as that around the Co atoms in Co_2Al_9 (Douglas, 1950). Fig. 1 shows one half of the unit cell.

Table 1. *Parameters*

	$FeCu_2Al_7$			
	Westgren	This paper	T(CoCu)	Standard deviations
z_1	0·122	0·134	0·132	0·0008
z_2	0·300	0·2992	0·2970	0·0003
x_3	0·278	0·278	0·272	0·0006
y_3	0·092	0·088	0·088	0·0006
x_4	0·167	0·165	0·153	0·002
x_5	0·203	0·198	0·202	0·002
y_5	0·414	0·420	0·420	0·002
z_5	0·100	0·100	0·100	0·0008

The standard deviations of the parameters are the same for both $FeCu_2Al_7$ and T(CoCu), and are listed in the last column.

The Al-rich corner of the Co–Cu–Al system was investigated by Pfeil & Raynor (1949), who found three ternary phases, one of which, T(CoCu), entered into equilibrium with the Al-rich solid solution. Owing to experimental difficulties, no direct evidence was obtained for the composition of this phase, but by the extrapolation of two phase boundaries it was deduced that one Al-rich corner of the phase field had composition $Co_2Cu_5Al_{16}$. Pfeil & Raynor considered the ideal formula of T(CoCu) to be $Co_2Cu_5Al_{13}$, for this would give the three phases $FeCu_2Al_7$, T(CoCu), and $NiCu_3Al_6$ (Bradley & Lipson, 1936) about the same electron-to-atom (e/a) ratio, assuming Raynor's scheme of negative valencies for the transition metal atoms (i.e. Fe, 2·66; Co, 1·71; Ni, 0·61). The usual explana-

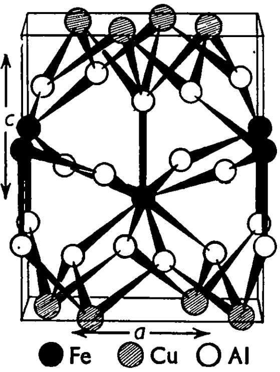

Fig. 1. One half of the unit cell of $FeCu_2Al_7$.

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tion of the occurrence of several compounds at the same e/a ratio is that they are all based on the same structure, which is one having a prominent Brillouin zone just able to contain that electron concentration. To discover whether such an explanation was valid for these ternary alloys the structure of T(CoCu) was determined, and the electron concentrations in T(CoCu) and $FeCu_2Al_7$ were found as accurately as possible. It was found that the two structures are isomorphous. Both were therefore accurately refined in the hope that the changes in atomic positions caused by replacing Fe by Co atoms might throw light on the nature of the interatomic forces in this type of compound.

2. The structure of T(CoCu)

(i) *Material*

Pfeil & Raynor were unable to obtain crystals of T(CoCu) because the presence of Cu in the slow-cooled ingots renders the usual method of electrolytic extraction almost useless. By modifying the technique, Dr A. R. Harding succeeded in 1953 in extracting about 10 mg. of the crystals, which he kindly gave us. The crystals were plate-like, having an irregular and sometimes dendritic appearance. A chemical analysis by Messrs Johnson, Matthey and Company, Limited, gave the composition:

Cu: 34·3±1·0; Co: 13·0±1·0 wt.% (Al by difference).

Two possible formula units are $Co_{0\cdot8}Cu_{1\cdot9}Al_7$ and $Co_2Cu_{4\cdot9}Al_{17\cdot7}$.

With such a small quantity of material it was not possible to determine the density by displacement, and the density was too high for the flotation method to be satisfactory, although by using a hot Clerici's solution it was shown to lie between 4·0 and 4·4 g.cm.$^{-3}$. The high viscosity of the solution precluded a more accurate determination. Owing to the uncertainties in the composition and density, the exact contents of the unit cell cannot be calculated; this leads to difficulties in the interpretation of results, as will be shown later.

(ii) *Unit cell*

Single-crystal Laue and oscillation photographs showed the unit cell to be tetragonal, with Laue symmetry $4/mmm$. Accurate cell dimensions, found by the method of Farquhar & Lipson (1946), are:

$$a = 6{\cdot}3047 \pm 0{\cdot}0005,\ c = 14{\cdot}756 \pm 0{\cdot}001\ \text{Å}\,.$$
$$\text{Volume} = 586{\cdot}5 \pm 0{\cdot}1\ \text{Å}^3\,.$$

Systematic absences indicate that the space-group is $P4nc$ or $P4/mnc$. The similarity of the cell size and symmetry of T(CoCu) to those of $FeCu_2Al_7$ suggests that the two structures are isomorphous, and this was later verified by intensity measurements.

(iii) *Structure*

All the atomic parameters of the $FeCu_2Al_7$ structure can be obtained from a projection on (100), in which the atoms are well resolved. ($h0l$) reflexions from a crystal of T(CoCu) with a cross-section of side 0·035 mm. were recorded on a zero-layer Weissenberg photograph, using filtered Mo $K\alpha$ radiation and a multiple-film pack. Reflexions could be seen out to $\sin\theta/\lambda = 1{\cdot}0$, and the 63 non-zero intensities were estimated visually. Correction was made for polarization and Lorentz factors, but not for absorption. The linear absorption coefficient is about 100 cm.$^{-1}$ for Mo $K\alpha$ radiation.

The corrected intensities agreed well with those calculated from the Westgren $FeCu_2Al_7$ structure, with Co in place of Fe, using Viervoll & Ögrim (1949) scattering factors. Accurate parameters were found by the use of F_o and F_o-F_c Fourier projections, F_c being scaled to F_o. The final parameters are given in Table 1. Lists of F_o and F_c are available in a thesis (Bown, 1955). The agreement index R is 0·083. Interatomic distances are listed in Table 2.

With Mo $K\alpha$ radiation it is not possible to distinguish directly between Co and Cu atoms, since the atomic scattering factors differ by only about 2 units. The interatomic distances indicate that the smaller Co atoms are in the H position, rather than in A or B. This was to some extent confirmed by experiments with Co $K\beta$ radiation, for which dispersion increases the difference between the f curves to about 4 units. The measured intensity ratios of selected pairs of neighbouring reflexions (e.g. 2·7±0·3, for 202:101 and

Table 2. *Interatomic distances*

All values are in Ångström units.
The differences shown in the last column have less than 1% chance of being due to random error.
TM stands for transition metal atom, either Fe or Co.

		$FeCu_2Al_7$	T(CoCu)	Standard deviation	Significant differences
Cu	2Cu	2·613	2·549	0·007	0·064
	1Cu	3·026	3·082	0·012	−0·056
	$2Al_{16}$	2·511	2·528	0·015	—
	$2Al_{16}$	2·522	2·543	0·015	—
	$2Al_{16}$	2·625	2·599	0·016	—
	$2Al_4$	2·717	2·652	0·011	0·065
TM	$4Al_{16}$	2·483	2·468	0·015	—
	$4Al_8$	2·477	2·489	0·007	—
	$1Al_4$	2·456	2·434	0·016	—
Al_4	$4Al_{16}$	2·985	2·976	0·015	—
	$4Al_8$	2·928	2·957	0·012	−0·029
Al_8	$2Al_{16}$	2·726	2·674	0·019	0·052
	$2Al_{16}$	2·888	2·933	0·021	—
	$2Al_{16}$	3·259	3·181	0·021	0·077
	$1Al_8$	2·957	2·728	0·034	0·229
	$4Al_8$	3·346	3·381	0·012	−0·035
Al_{16}	$1Al_{16}$	2·706	2·740	0·030	—
	$2Al_{16}$	2·799	2·754	0·015	0·045
	$1Al_{16}$	2·974	2·951	0·030	—

4·4±0·5 for 103:204) agreed with those calculated assuming Co atoms in the *H* sites (2·6, 5·0), but not with those calculated assuming that the Cu and Co atoms were randomly distributed over sites *A*, *B* and *H* (6·2, 7·7).

The refinement has been carried out assuming a formula unit $CoCu_2Al_7$, and this is certainly the ideal structural composition of *T*(CoCu). The chemical analysis of the crystals used was $Co_{0.8}Cu_{1.9}Al_7$. This analysis may be incorrect either because of the very small quantity of material used, or because the crystals may have contained free Cu and Al. On the other hand, the analysis agrees quite well with Pfeil & Raynor's work. If the analysis is correct the simplest assumption would be that only 80% of the Co sites are occupied by Co atoms, the remainder being left vacant. This would, however, give rise to a hollow at the Co position in the $F_o - F_c$ syntheses, which was not observed. To make sure of this, an attempt was made to refine the structure assuming the Co site only 80% occupied. The resulting difference map showed a positive peak, about twice as high as any other, at the Co position, and increased negative regions round the other atoms. These features could not be removed by moving the atoms, nor could the *R* factor be reduced from its increased value of 0·135. The Co positions are therefore certainly not 20% vacant, so that, if the chemical analysis is correct, some other atoms have replaced Co atoms. A deficiency of less than 10% in the heavy-atom sites could not be detected with certainty. Which of the several possible schemes of replacement actually takes place is not known but in no case would the extent of replacement be more than about 10%. It is estimated that this amount of replacement might cause changes in interatomic distances of about 0·01 Å from those to be expected for the structure corresponding to the ideal formula $CoCu_2Al_7$.

3. Refinement of the $FeCu_2Al_7$ structure

(i) *Material*

The crystals used in this work were kindly given to us by Mr B. Ward. They were in the form of thin plates parallel to (001). The composition of the crystals, obtained spectrographically by the Admiralty Materials Laboratory, was:

Fe: 15·4; Cu: 33·9; Al: 50·7 wt.%,

giving a formula unit $FeCu_{1.9}Al_{6.7}$. The density, measured by displacement, was 4·30±0·08 g.cm.$^{-3}$.

(ii) *Unit cell*

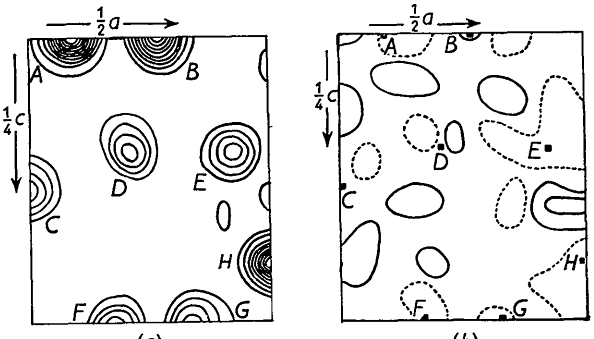
Laue and oscillation photographs of single crystals confirmed the unit cell and Laue symmetry of the space group *P4/mnc* found by Westgren. The cell dimensions determined by the method of Farquhar & Lipson (1946) are:

$$a = 6.336 \pm 0.001,\ c = 14.870 \pm 0.002\ \text{Å}.$$
$$\text{Volume} = 597.0 \pm 0.2\ \text{Å}^3.$$

(iii) *Refinement of the structure*

(*h0l*) reflexions were recorded on a zero-layer Weissenberg photograph from a crystal of length 0·1 mm. along the rotation axis and a cross-section approximately 0·04 mm. square. Filtered Mo *Kα* radiation and a multiple-film pack were used. The intensities of the spots up to sin $\theta/\lambda = 0.8$ were estimated visually and corrected for Lorentz and polarization factors but not for absorption or extinction.

The projection of the structure on (010) was refined using F_o and $F_o - F_c$ syntheses. The final syntheses are shown in Fig. 2; the agreement index *R* is 0·081. The final values of the parameters with their standard deviations are given in Table 1. Interatomic distances are listed in Table 2.



(*a*) (*b*)

Fig. 2. $FeCu_2Al_7$, 010 projection: (*a*) final F_o synthesis; (*b*) final $F_o - F_c$ synthesis.

The contour intervals in the $F_o - F_c$ synthesis are one-fifth of those in the F_o. Negative contours are shown as broken lines.

4. Discussion

(i) *Brillouin zone*

Of Pfeil & Raynor's three ternary phases, two have the same structure, but the Ni phase has been shown to have a different structure (Bown, 1956). It might be supposed that the Fe and Co phases are electron compounds, and that the Ni alloy phase occurs at the same *e/a* ratio by chance. The prominent Brillouin zone of the $FeCu_2Al_7$ structure has been calculated by Black (1955); the inscribed sphere contains 55·3, and the full zone 71·4 electrons per cell. The zone for *T*(CoCu) is almost identical. The calculated electron concentration, using Raynor's negative valencies, is 91±3 electrons per cell for the $FeCu_2Al_7$ crystals used in the refinement, and for *T*(CoCu), taking the lowest possible density and the analysed composition, it is at least 85·1 electrons per cell. The range of composition of $FeCu_2Al_7$ is probably small and it is likely that the Brillouin zone is overlapped for all compositions.

There is thus no doubt that this Brillouin zone is considerably overlapped, and there is no other prominent zone. It is therefore probable that these phases should not be classed as electron compounds.

(ii) *Interatomic distances*

Table 2 is a list of interatomic distances for the two compounds. The differences between these have been tested for significance by the method suggested by Cruickshank (1949). Some mean distances are shown in Table 3.

Table 3. *Mean contact distances*

(Only interatomic distances less than 3 Å included)

	$FeCu_2Al_7$	T(CoCu)
TM–Al	2·477 Å	2·474 Å
Cu–Al	2·594	2·580
Al–Al	2·865	2·851

Inspection of Tables 2 and 3 shows that the distances in the two structures are very similar, there being only one difference of more than 0·08 Å in an individual distance, and the mean distances differing by 0·015 Å at most. This may be taken to show that if the *TM**–Al interactions have a strong effect in determining the structure, the Fe–Al and Co–Al bonds are remarkably similar both in strength and in angular disposition.

The unit cell of T(CoCu) is significantly smaller than that of $FeCu_2Al_7$. The mean distances show that this contraction is taken up mainly by contractions of Al–Al and Cu–Al distances and not by changes in *TM*–Al distances. These differences in distance may be qualitatively explained by atomic displacement in T(CoCu), at least in part, as follows. The mean Co–Al distance agrees perfectly with that observed in Co_2Al_9 and Co_2Al_5, although it has already been concluded that there must be some replacement of Co atoms in the crystals examined. Al is unlikely to replace Co; a possible situation is that about 10% of the Co sites are occupied by Cu atoms, a further 10% being left vacant. The expansion and contraction arising as a consequence of these replacements would oppose one another, leaving the mean Co–Al distance approximately unchanged, as found. The formula unit can then be written $(Co_{0\cdot8}Cu_{0\cdot1})Cu_{1\cdot8}Al_7$. The observed differences in mean Cu–Al distance would be due to the random vacancies for T(CoCu). Changes are also observed in the Al–Al distances; these may be due, in part, to the rearrangement caused by substitution in the Co site. The relatively large difference of 0·23 Å in the Al_8–Al_8 distance is not readily explained in this manner. It may be, however, that the energy change associated with a change of this distance is less than that for changes of the other Al–Al bond lengths, since it is the only Al–Al contact which is not an edge of a polyhedron of Al atoms about either a *TM* or a Cu atom.

This explanation of the small differences in interatomic distances is only tentative, and assumes that the chemical analysis of T(CoCu) is correct. It is unfortunate that the defects in the T(CoCu) structure are sufficient to mask a possible difference in Al–Al distances due to another cause. If the *TM* atoms absorbed electrons from the Al atoms there should be an electrostatic repulsion between Al atoms, and if the electron absorption for Fe were greater than that for Co (as would be expected), then the average Al–Al distance would be longer in $FeCu_2Al_7$ that in $CoCu_2Al_7$. This effect would probably be most pronounced for the Al_8–Al_8 distance, since each Al_8 atom is bonded to two *TM* atoms. Such changes in the Al_8–Al_8 distance and in the average Al–Al distance were found, but may have been caused by defects in the T(CoCu) structure, as explained above. A test of the electrostatic repulsion theory must therefore await a more favourable case.

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* *TM* stands for transition metal atom, either Fe or Co.

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