

# The Structure of the $\zeta$ -phase in the Transition Metal-Zinc Alloy Systems

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The structure of the  $\zeta$ -phases formed in the alloy systems Mn-Zn, Fe-Zn, and Co-Zn has been determined; the structure is described and the most probable position for the transition metal atoms is postulated. The three compounds are compared in detail and the small differences between their structures are discussed.

## 1. Introduction

Schramm (1937, 1938, 1940) has shown that in each of the alloy systems Mn-Zn, Fe-Zn and Co-Zn the intermediate phase most rich in zinc is formed peritectically and contains approximately 93 at.% of zinc. Götzel *et al.* (1941) also showed that these three compounds which were named  $\zeta$ -phases are isomorphous; they determined the lattice parameters which are given in Table 1, and showed that the possible space groups are  $C2$ ,  $Cm$  and  $C2/m$ .

Table 1. Cell dimensions of the three  $\zeta$ -phases

Values found by Götzel <i>et al.</i>			
	CoZn <sub>13</sub>	FeZn <sub>13</sub>	MnZn <sub>13</sub>
<i>a</i>	13.46 kX.	13.65 kX.	13.65 kX.
<i>b</i>	7.49	7.61	7.61
<i>c</i>	5.06	5.10	5.10
$\beta$	127° 5'	128° 44'	128° 44'
Values found in the present investigation			
	CoZn <sub>13</sub> (Å)	FeZn <sub>13</sub> (Å)	MnZn <sub>13</sub> (Å)
<i>a</i>	13.306 ± 0.033	13.424 ± 0.005	13.483 ± 0.005
<i>b</i>	7.535 ± 0.002	7.6080 ± 0.001	7.6626 ± 0.001
<i>c</i>	4.992 ± 0.012	5.061 ± 0.003	5.134 ± 0.003
$\beta$	126° 47' ± 15'	127° 18' ± 2'	127° 47' ± 2'

The object of the work described here has been to determine the general structure of the three compounds; to refine each of them with sufficient precision to enable detailed comparisons to be made; and thus to obtain information about the changes in atomic environment brought about by a change in the atomic number of the transition metal.

## 2. Material

The crystals used in this investigation were extracted electrolytically from ingots containing more than 99% wt. of zinc. Many of the crystals extracted by

this means, although showing well developed faces, gave very broad X-ray reflexions. The broadening of the reflexions was roughly proportional to the crystal size, and appears to arise because the range of misorientation between the crystallites of the mosaic structure is rather greater than is usual.

Analyses of extracted crystals giving very broad reflexions always gave a composition richer in the transition metal than the compositions given by Schramm. This probably indicated that the alloy from which the crystals were extracted was not truly in equilibrium, and these crystals probably contain a small proportion of a second phase, either as cores or else in the boundaries of the crystal mosaic. By using very dilute alloys and long heat treatments it was found possible to obtain crystals of the manganese and iron phases which gave sharp reflexions. No very good crystals of the cobalt phase were ever prepared. The extracted crystals of all three phases were in the form of long needles whose axis was parallel to [001]; the needles were of rhombic cross section, the faces developed being the form (110).

Hartmann *et al.* (1955) reported a zinc-rich chromium phase crystallizing in the form of needles of rhombic section with the lattice constant parallel to the needle axis equal to 5.23 kX. and it seemed probable that this would prove to be yet another  $\zeta$ -phase. Accordingly in order to investigate this possibility an alloy was prepared containing 5% wt. of chromium; after about one week's heat treatment under argon at 500–550 °C. the chromium had dissolved and crystals were extracted from the slowly cooled ingot. By far the major part of the extracted crystals were thin hexagonal platelets which are presumably of the previously reported hexagonal intermediate phase. A few very thin needle-shaped crystals were also extracted and these were shown by X-ray diffraction to be isomorphous with the other  $\zeta$ -phases. The small size of these crystals, however, precluded the complete structure analysis, nor were sufficient crystals obtained for chemical analysis. Further investigation is therefore needed to show whether or not this is a true equilibrium binary phase.

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### 3. Unit cell and space group

Laue, oscillation and Weissenberg photographs confirmed the monoclinic classification of the  $\zeta$ -phases given by Schramm. The cell dimensions which were determined for the crystals used in the structure refinements are given in Table 1. Those for the manganese and iron phases were determined by a combination of the methods due to Farquhar & Lipson (1946) and Weisz, Cochran & Cole (1948). Because of the broad reflexions the Weisz, Cochran & Cole method could not be used for the cobalt-zinc crystals and for this reason, and also because of the paucity of strong reflexions of suitable spacing in the [010] zone, the  $a$ ,  $c$  and  $\beta$  parameters for this phase are not known with great accuracy.

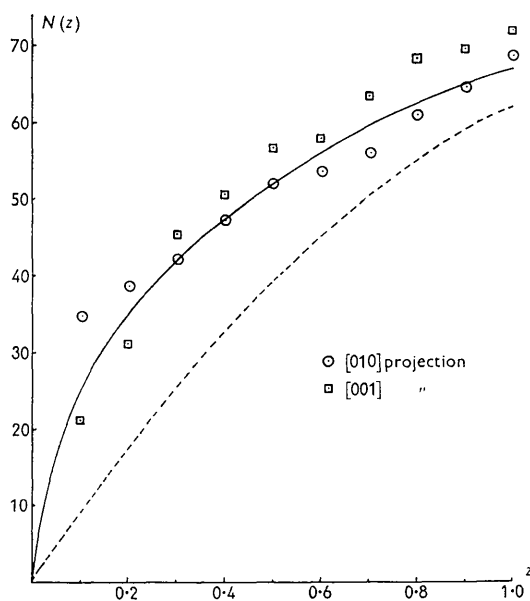


Fig. 1. Tests for centrosymmetry of the [010] and [001] projections of the structure of  $\text{CoZn}_{13}$ .

The three possible space groups for the  $\zeta$ -phase are  $C2$ ,  $Cm$  and  $C2/m$ . Statistical tests were applied to the intensity data from the [001] and [010] zones of the cobalt-zinc phase and the distribution curves obtained are shown in Fig. 1. These were taken to show that both these projections were centrosymmetric and hence that the proper space group is  $C2/m$ .

### 4. Contents of the unit cell

The volume of the unit cell of the  $\zeta$ -phase is approximately  $400 \text{ \AA}^3$ , and the density of the cobalt-zinc phase which was measured by displacement is  $7.0 \pm 0.2 \text{ g.cm.}^{-3}$ . The mass of the contents of the unit cell is therefore  $1680 \pm 50 \text{ A.M.U.}$  Using the composition found by Schramm (1938) this gives 26 zinc atoms and 2 cobalt atoms per unit cell.

### 4. Determination of the structure

The  $y$  axis of the structure which is of length  $7.54 \text{ \AA}$  is intersected at heights 0 and  $\frac{1}{2}$  by mirror planes. The atoms in the structure, if they are to have their normal radii, must lie either on these planes or at least  $1.3 \text{ \AA}$  away from them. The  $y$  coordinates of the atoms are therefore restricted to the values 0 and  $\frac{1}{2}$  or to the ranges  $0.17\text{--}0.33$  and  $0.67\text{--}0.83$ ; the atoms accordingly lie in alternate flat and puckered layers perpendicular to the  $y$  axis. The relative numbers of atoms in the flat and puckered layers were determined by means of a one-dimensional Fourier projection on

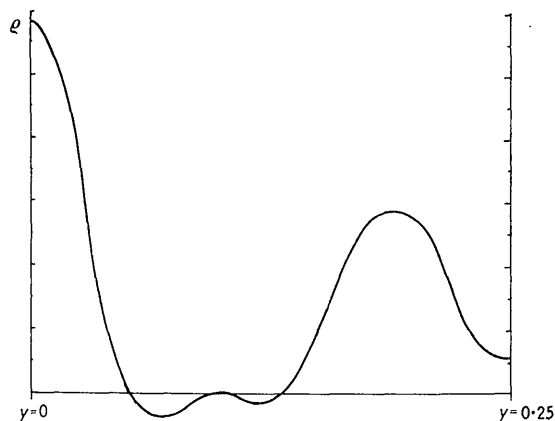


Fig. 2. One-dimensional projection of the structure on [010].

[010]. The signs of the  $0k0$  structure amplitudes were chosen to give a positive peak at the origin and no further positive peak within  $1.3 \text{ \AA}$  of this. Only one combination of signs satisfied these two conditions; the projection is shown in Fig. 2. From the ratio of the areas under the two peaks in this projection the number of atoms in the flat layers of the structure was deduced as twelve, i.e. six in each layer. The narrow composition range of the  $\zeta$ -phase suggests that the structure is highly ordered, so that the two transition metal atoms in each cell must lie on centres of symmetry say  $2(a)$  positions. With this in mind and knowing the numbers of atoms in the flat and puckered layers, consideration of the packing requirements enabled an approximate structure to be put forward. The positions of the atoms in this structure were:

$A$	2 T.M. or 2 $\text{Zn}_0$	in $2(a)$ $(0, 0, 0)$
$C$	2 $\text{Zn}_0$ or 2 T.M.	in $2(c)$ $(0, 0, \frac{1}{2})$
$I_1$	4 $\text{Zn}_1$	in $4(i)$ $(x_1, 0, z_1)$
$I_2$	4 $\text{Zn}_2$	in $4(i)$ $(x_2, 0, z_2)$
$J_3$	8 $\text{Zn}_3$	in $8(j)$ $(x_3, y_3, z_3)$
$J_4$	8 $\text{Zn}_4$	in $8(j)$ $(x_4, y_4, z_4)$

The values of the positional parameters of the structure are given in Table 2.

The atoms in this proposed structure are resolved

Table 2. Atomic parameters of the  $\zeta$ -phases

Parameter	CoZn <sub>13</sub>	FeZn <sub>13</sub>	MnZn <sub>13</sub>	Standard deviation	Parameters of trial structure
$x_1$	0.1110	0.1120	0.1155	0.0005	0.10
$z_1$	0.2920	0.2920	0.2910	0.002	0.31
$x_2$	0.2190	0.2195	0.2232	0.0005	0.21
$z_2$	0.0770	0.0730	0.0735	0.002	0.19
$x_3$	0.0780	0.0770	0.0750	0.0005	0.10
$y_3$	0.2975	0.2920	0.2920	0.0007	0.31
$z_3$	0.8340	0.8350	0.8330	0.001	0.83
$x_4$	0.1765	0.1760	0.1744	0.0005	0.18
$y_4$	0.1765	0.1780	0.1810	0.0007	0.19
$z_4$	0.5530	0.5450	0.5485	0.001	0.56

in both the [001] and [010] projections, and accordingly data from these projections were used to confirm the structure and in the structure refinements.

### 5. Refinement of the structures

The reflexions from the [010] and [001] zones of the three  $\zeta$ -phases were recorded on normal-beam Weissenberg photographs using Mo  $K\alpha$  radiation with multiple films. The intensities were estimated by visual comparison with an intensity scale and were corrected for the Lorentz, polarization and absorption effects. The absorption factors were calculated by the digital computer EDSAC II, using the programme devised by Wells (1960). The temperature factor and the effect of resolution of the  $\alpha_1, \alpha_2$  doublet were taken into account by scaling the observed structure amplitudes to those calculated, in regions of  $\sin \theta/\lambda$ . Intensities for the cobalt-zinc phase could be measured only out to  $\sin \theta/\lambda = 0.8 \text{ \AA}^{-1}$  for the other two phases measurements were made out to  $\sin \theta/\lambda = 1.0 \text{ \AA}^{-1}$ .

Using the positions of the trial structure and giving all the atoms equal weight, the structure factors for both projections were calculated to  $\sin \theta/\lambda = 0.5 \text{ \AA}^{-1}$  and compared with the observed structure amplitudes of the CoZn  $\zeta$ -phase; a fair degree of agreement was observed and after appropriate scaling the agreement index was 0.40. The  $F_o$  syntheses calculated using the signs of the calculated structure factors showed the main features of the proposed structure and indicated some atomic shifts. From this point the structures were refined in both the [001] and [010] projections using  $F_o - F_c$  Fourier syntheses; the final  $R$ -factors were:

	[010]	[001]
CoZn	0.104	0.101
FeZn	0.121	0.098
MnZn	0.104	0.092

The final parameters are given in Table 2 and the final  $F_o$  syntheses for the manganese zinc phase are shown in Fig. 3. Fig. 4 shows the final  $F_o - F_c$  synthesis for the [010] projection of the FeZn phase; it will be noted that the agreement for this projection is significantly less good than for the others and this disagreement shows up in the synthesis as a negative

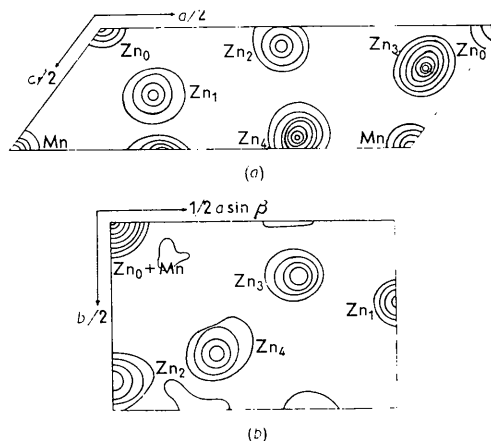


Fig. 3. (a) Final [010] projection of the structure of MnZn<sub>13</sub>. (b) Final [001] projection of the structure of MnZn<sub>13</sub>. Positive contours have been drawn at equal arbitrary intervals.

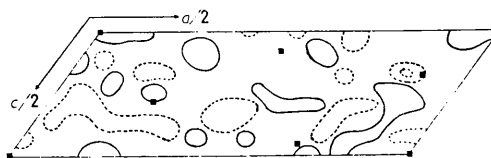


Fig. 4. Final  $F_o - F_c$  synthesis for FeZn<sub>13</sub> projected on (010). The contour intervals are one-fifth those of Fig. 3, negative contours are shown as broken lines, squares mark the atomic sites.

peak in the position of the Zn<sub>3</sub> atom which has positive areas on either side of it. This may be taken as evidence of an asymmetric temperature vibration of this atom or alternatively could be explained if the true space group of the structure were less symmetric than  $C2/m$ . The accuracy of the data does not however justify any definite conclusions and any deviation from centrosymmetry is certainly small.

It has not been possible to identify the transition-metal atoms from the peak heights on the electron-density projections. These are almost certainly located on one of the centres of symmetry of the structure and it is at these points that the greatest errors in the electron density occur.

## 6. Description of the structure

Table 3 gives the mean interatomic distances for the six independent atoms of the structure. It can be seen that in all three phases the mean of the interatomic distances for the atoms in the 2(c) positions is significantly shorter than that of any of the others, which provides strong evidence for locating the transition metal atoms on this site. The atoms in these sites

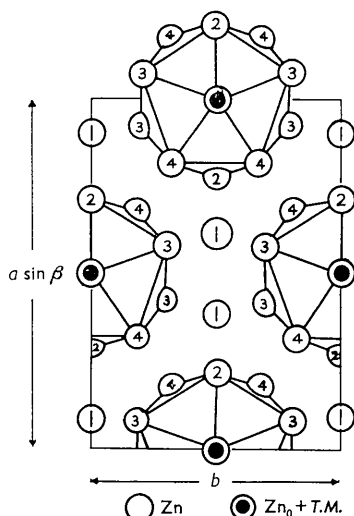


Fig. 5. Schematic drawing of the structure viewed down [001].

Table 3. Mean interatomic distances in the three  $\zeta$ -phases

Values are in Å, limits $\pm 0.005$ Å			
Position	CoZn <sub>13</sub>	FeZn <sub>13</sub>	MnZn <sub>13</sub>
2(a)	2.688	2.695	2.724
2(c)	2.575	2.591	2.605
Zn <sub>1</sub>	2.651	2.673	2.686
Zn <sub>2</sub>	2.738	2.766	2.779
Zn <sub>3</sub>	2.720	2.739	2.748
Zn <sub>4</sub>	2.704	2.724	2.735

are surrounded by twelve zinc atoms at the vertices of a slightly distorted icosahedron; the icosahedra link together sharing one pair of opposite vertices, the Zn<sub>0</sub> atoms, to form chains parallel to the *c* axis. These chains pack together in an approximately hexagonal array, and the Zn<sub>1</sub> atoms fit into the interstices between chains. The arrangement is illustrated in Fig. 5.

## 7. Discussion

A complete list of the interatomic distances in the three compounds is given in Table 4. The shortest interatomic distance in the structures is that between the transition metal atom and Zn<sub>0</sub>, this distance is in all cases significantly shorter than the sum of the 12-coordinated radii of the atoms. The Zn<sub>0</sub> atom is the only zinc atom in the structure which is in contact with two transition metal atoms and the fact that this distance is an abnormally short one, and that the Zn<sub>0</sub> atom lies on the straight line joining the two transition

Table 4. Interatomic distances in the three  $\zeta$ -phases

Atom	Neighbour	CoZn <sub>13</sub>	FeZn <sub>13</sub>	MnZn <sub>13</sub>	Standard deviation	Other neighbours
T.M.	2 Zn <sub>0</sub>	2.496	2.530	2.567	0.006	
	2 Zn <sub>2</sub>	2.594	2.595	2.620	0.011	
	4 Zn <sub>3</sub>	2.609	2.599	2.614	0.009	
	4 Zn <sub>4</sub>	2.571	2.610	2.607	0.009	
Zn <sub>0</sub>	2 Zn <sub>2</sub>	2.701	2.738	2.794	0.011	2 T.M.
	4 Zn <sub>3</sub>	2.796	2.783	2.797	0.009	
	4 Zn <sub>4</sub>	2.671	2.669	2.695	0.009	
Zn <sub>1</sub>	1 Zn <sub>1</sub>	2.628	2.647	2.687	0.022	
	1 Zn <sub>2</sub>	2.550	2.576	2.584	0.016	
	2 Zn <sub>3</sub>	2.674	2.716	2.745	0.012	
	2 Zn <sub>3</sub>	2.558	2.591	2.606	0.012	
	2 Zn <sub>4</sub>	2.782	2.787	2.787	0.012	
	2 Zn <sub>4</sub>	2.653	2.654	2.658	0.012	
Zn <sub>2</sub>	2 Zn <sub>3</sub>	2.895	2.940	2.928	0.012	1 T.M., 1 Zn <sub>0</sub> ,
	2 Zn <sub>3</sub>	2.700	2.693	2.738	0.012	1 Zn <sub>1</sub>
	2 Zn <sub>4</sub>	2.865	2.902	2.892	0.012	
	2 Zn <sub>4</sub>	2.675	2.725	2.729	0.012	
	2 Zn <sub>4</sub>	3.057	3.094	> 3.2	0.012	
Zn <sub>3</sub>	1 Zn <sub>3</sub>	2.671	2.697	2.703	0.014	1 T.M., 1 Zn <sub>0</sub> ,
	1 Zn <sub>3</sub>	3.052	3.165	3.187	0.014	2 Zn <sub>1</sub> , 2 Zn <sub>2</sub>
	1 Zn <sub>4</sub>	2.845	2.878	2.896	0.010	
	1 Zn <sub>4</sub>	2.862	2.840	2.792	0.010	
	1 Zn <sub>4</sub>	3.130	3.105	3.159	0.010	
	1 Zn <sub>4</sub>	2.592	2.652	2.655	0.010	
Zn <sub>4</sub>	1 Zn <sub>4</sub>	2.564	2.540	2.601	0.014	1 T.M., 1 Zn <sub>0</sub> , 2 Zn <sub>1</sub> ,
	1 Zn <sub>4</sub>	2.660	2.709	2.774	0.014	3 Zn <sub>2</sub> , 4 Zn <sub>3</sub>

Values are in Ångström units; T.M. stands for transition metal: Mn, Fe or Co.

metal atoms is in accordance with findings for aluminium rich alloys of transition metals (Brown, 1959).

Examination of Table 4 shows that in very few cases are the differences in interatomic distances between the three structures large enough to be significant. However a significant trend can be deduced from the list of mean distances (Table 3), which shows that as the atomic number of the transition metal atom is reduced on passing from  $\zeta$ -CoZn to  $\zeta$ -MnZn, the mean radii of all the atoms in the structure increase. It is of interest that this effect is exhibited to much the same extent by all the atoms in the structure and not principally by the transition metal atoms. It may be taken as evidence that *d*-electrons from the transition metal atoms participate not only in bonds with their immediate neighbours but contribute to the bonding of the structure as a whole.

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## Short Communications

*Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

*Acta Cryst.* (1962). **15**, 612

**Zur Bestimmung der Betragsquadrate von Strukturfaktoren aus Texturaufnahmen.** Von HANS-JOACHIM BUNGE, *Institut für Strukturforschung der Deutschen Akademie der Wissenschaften zu Berlin, Deutschland*

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Die zur Strukturbestimmung benötigten Betragsquadrate der Strukturfaktoren werden im allgemeinen aus Messungen an Einkristallen gewonnen. In manchen Fällen stehen jedoch keine Einkristalle zur Verfügung. Man muss dann polykristallines Material verwenden. Da hierbei die Kristallite gewisse Vorzugsorientierungen besitzen können, hängt die in einer bestimmten Richtung reflektierte Intensität ausser von der Kristallstruktur auch von der als Textur bezeichneten Orientierungsverteilung der Kristallite ab. Darüber hinaus treten 'Koinzidenzen' symmetrisch ungleichwertiger Reflexe auf, so dass die entsprechenden Strukturfaktoren nicht einzeln erhalten werden können. Die dadurch bedingten Schwierigkeiten können jedoch durch quantitative Berücksichtigung der Orientierungsverteilung der Kristallite überwunden werden. Je nach der Art der speziellen Textur treten verschiedene Probleme in den Vordergrund. Die verhältnismässig scharfen Texturen liefern Reflexe, die denen der Einkristalle ähnlich sind, nur sind sie durch die Textur verbreitert. Um an solchen 'Kristallen' Strukturfaktoren bestimmen zu können, ist es günstig, den Zusammenhang zwischen den texturbedingten Verbreiterungsfunktionen der einzelnen Reflexe quantitativ zu beherrschen. Bei den verhältnismässig schwachen Texturen dagegen sind die Reflexe so stark verbreitert, dass sie vielfach ineinander übergehen. Hier

wird also das genannte Problem der Koinzidenzen wichtig. Wir wollen im folgenden eine Methode zur rechnerischen Behandlung dieser Probleme andeuten.

Eine ausführlichere Darstellung ist an anderer Stelle gegeben worden (Bunge, 1961b).

Wie früher gezeigt wurde, lässt sich die Orientierungsverteilung durch eine Verteilungsfunktion  $C(\mathfrak{h}, \mathfrak{\eta})$  beschreiben, die angibt, für welchen Bruchteil des Gesamtvolumens der Probe die Kristallrichtung  $\mathfrak{h}$  mit der Richtung  $\mathfrak{\eta}$  der Probe zusammenfällt. Die Richtung  $\mathfrak{h}$  ist also bezüglich der kristallographischen Achsen festgelegt, die Richtung  $\mathfrak{\eta}$  dagegen bezieht sich auf ein mit der Probe fest verbundenes Koordinatensystem. Es ist klar, dass diese Verteilungsfunktion bezüglich der Kristallrichtung  $\mathfrak{h}$  der Symmetrie der betreffenden Kristallite genügen muss. Die Texturverteilung kann aber auch bezüglich der Probe und damit also der Variablen  $\mathfrak{\eta}$  eine bestimmte Symmetrie besitzen. Diese kann beispielsweise bei Fasertexturen die Rotationssymmetrie sein. Eine Funktion einer Richtung im Raum, die der Symmetrie einer bestimmten Punktsymmetriegruppe genügt, kann in eine Reihe nach Kugelflächenfunktionen entwickelt werden, die selbst die betreffende Symmetrie besitzen (Meyer, 1954; Laporte, 1948). Eine Funktion von zwei solchen Variablen  $\mathfrak{h}$  und  $\mathfrak{\eta}$  kann in eine zweifache Reihe solcher Kugelfunktionen entwickelt werden. Im Falle einer