

## The Crystal Structure of $Mg_{51}Zn_{20}$

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The crystal structure of  $Mg_{51}Zn_{20}$ , a phase designated conventionally as " $Mg_7Zn_3$ ," has been determined by the single-crystal X-ray diffraction method. It was solved by the examination of a Patterson synthesis, and refined by the ordinary Fourier and least-squares method; the  $R$  value obtained was 4.8% for 1167 observed reflections. The crystal is orthorhombic, space group  $Immm$ , with  $a = 14.083(3)$ ,  $b = 14.486(3)$ ,  $c = 14.025(3)$  Å, and  $Z = 2$ . There are 18 independent atomic sites, Zn1–Zn6, Mg1–Mg10, A, and B, and the last two sites are statistically occupied by Zn and Mg atoms with the occupancies;  $0.46(2)Zn7 + 0.52(2)Mg11$  and  $0.24(2)Zn8 + 0.74(2)Mg12$ , for A and B, respectively. The structure of the crystal is described as an arrangement of icosahedral coordination polyhedra, to which all the atomic sites but Zn3 site belong. In this arrangement the Zn atoms other than the Zn3 and Zn8(B) center the icosahedral coordination polyhedra with coordination number 12. The Zn3, Zn8 atoms, and all the Mg atoms except Mg11(A) are located at the centers of various coordination polyhedra with the coordination numbers from 11 to 15. The distances between neighboring atoms are 2.71–3.07, 2.82–3.65, and 2.60–3.20 Å for Zn–Zn, Mg–Mg, and Zn–Mg, respectively.

### Introduction

In view of considerable current interest in amorphous alloys, Mg–Zn system is particularly favorable in many respects. Until recently amorphous alloys which were stable at room temperature were composed of several elements at least one of which was a transition or noble metal element. Now it has become possible to make stable amorphous alloys with only two components both of which are simple metals. Such systems are highly desirable for theoretical and experimental studies of a wide variety of fundamental properties. One such sys-

tem is Mg–Zn system (1, 2). The composition range of interest is near eutectic at about 30 at% Zn, a phase designated conventionally as " $Mg_7Zn_3$ " in reference books of the phase diagrams (3, 4). Although some studies (5–7) of the eutectoid transformation of this phase were reported, the crystal structure itself has not been determined. For understanding amorphous states it is naturally of great help to know properties of the state to which the amorphous state crystallizes, or the crystallized phase of the same composition. Therefore the exact knowledge of the crystal structure of " $Mg_7Zn_3$ " phase is indispensable.

## Experimental

The alloy containing 30 at% Zn was prepared from accurately weighed quantities of magnesium and zinc of 3N purity by melting in a carbon crucible in an induction furnace. The obtained ingot encapsulated in Pyrex glass tube was annealed at  $335 \pm 2^\circ\text{C}$  for 48 hr and then quenched into water. The heat-treated ingot was cut into several pieces by a spark erosion cutter and etched for metallographic studies to find well grown grains. The specimens for X-ray and chemical analyses were obtained by cracking one of the well grown grains. Oscillation, Weissenberg, and precession photographs showed the Laue symmetry *mmm*. As the only systematic absences observed were those of reflexions for which  $h + k + l$  is odd, the lattice was established as body-centered orthorhombic, and the possible space groups were *I222*, *I2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>*, *Immm*, or *Immm*. The crystal data and the result of the chemical analysis are shown in Table I. The lattice constants were measured with a

single-crystal diffractometer. The wavelength used was  $0.70926 \text{ \AA}$  for  $\text{MoK}\alpha_1$  radiation. The density was determined by the Archimedes method using a crystal having a volume of about  $0.4 \text{ cm}^3$ .

For the intensity measurements, a nearly cubic specimen with side lengths of  $0.06\text{--}0.08 \text{ mm}$  was used. The reflections with  $0 \leq h \leq 21$ ,  $0 \leq k \leq 21$ , and  $0 \leq l \leq 18$ , for which  $2\theta < 60^\circ$ , were measured by using the Rigaku-Denki four-circle automated diffractometer with  $\text{MoK}\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) monochromated with a graphite monochromator. A  $2\theta - \omega$  scan mode at a rate of  $2^\circ$  (in  $\omega$ )/min was used. The background counts of 10 sec were measured on each side of the scanning width, which was monotonically increased with  $2\theta$  according to  $\Delta\theta = 1 + 0.5 \tan \theta$ . The reflections with  $F_0 < 10\sigma_{F_0}$  were measured twice and taken as the average. In order to check the stabilities of the diffractometer and crystal setting, three standard reflections were examined after each of all 100 reflections had been measured. The results showed no noticeable variations during the measurements. The intensities were corrected for the Lorentz and polarization effects. No absorption ( $\mu = 90 \text{ cm}^{-1}$ ,  $\mu r_{\text{max}} = 0.36$ ) or extinction corrections were made. Reflections with  $F_0 < 2.5\sigma_{F_0}$  were excluded from the data and a total of 1167 independent  $F_0$  values was used in the structure analysis.

## Determination and Refinement of the Structure

Refinement of the structure was performed by the block-diagonal least-squares method. The unit weight was given to all the reflections. The atomic scattering factors were those given in the International Tables for X-ray Crystallography (1974) (8). All the calculations for the structure analysis were made by the program

TABLE I  
CRYSTAL DATA AND CHEMICAL ANALYSIS<sup>a</sup>

Crystal system	Orthorhombic
<i>a</i> ( $\text{\AA}$ )	14.083(3)
<i>b</i> ( $\text{\AA}$ )	14.486(3)
<i>c</i> ( $\text{\AA}$ )	14.025(3)
Space group <sup>b</sup>	<i>Immm</i>
Chemical unit <sup>c</sup>	$\text{Mg}_{51}\text{Zn}_{20}$
$D_m$ ( $\text{g cm}^{-3}$ )	3.0
$D_x$ ( $\text{g cm}^{-3}$ )	3.0
<i>Z</i>	2
Mg(wt%)	49(1)
Zn	51(2)
Fe	<0.02
Cu	<0.01
Chemical composition	$\text{Mg}_{51(1)}\text{Zn}_{20(1)}$

<sup>a</sup> Atomic absorption spectrometry.

<sup>b</sup> Determined by the structure analysis.

<sup>c</sup> The chemical unit is 8 times the asymmetric unit  $\text{Mg}_{6.38(2)}\text{Zn}_{2.48(2)}$  determined by the structure analysis.

TABLE II  
FINAL ATOMIC COORDINATES, AVERAGE TEMPERATURE FACTORS, AND ANISOTROPIC TEMPERATURE FACTORS<sup>a</sup>

Atom	Site	x	y	z	$B_{av.}$ (Å <sup>2</sup> )
Zn1	8l	0	0.3389(1)	0.2066(1)	1.5
Zn2	8n	0.1621(1)	0.2869(1)	1/2	1.4
Zn3	8m	0.2055(1)	0	0.3323(1)	1.7
Zn4	4i	0	1/2	0.3051(2)	2.1
Zn5	4h	0	0.1729(2)	1/2	1.6
Zn6	2a	0	0	0	1.2
Zn7 <sup>b</sup>	8l	0	0.3355(3)	0.4002(3)	1.6
Zn8 <sup>b</sup>	8l	0	0.1698(5)	0.1096(5)	1.2
Mg1	16o	0.1116(3)	0.1812(2)	0.3065(3)	1.5
Mg2	16o	0.1815(3)	0.2846(2)	0.1177(3)	1.8
Mg3	16o	0.1926(3)	0.3914(2)	0.3114(3)	1.5
Mg4	8m	0.1068(3)	0	0.1731(3)	1.1
Mg5	8m	0.1097(4)	1/2	0.1193(4)	1.7
Mg6	8n	0.1803(3)	0.1029(3)	0	0.5
Mg7	8n	0.1830(4)	0.0975(3)	1/2	1.1
Mg8	4j	0	0	0.3848(6)	1.5
Mg9	4h	0	0.3521(6)	0	1.5
Mg10	4f	0.1148(6)	1/2	1/2	1.5
Mg11 <sup>b</sup>	8l	0	0.3463(6)	0.4011(6)	0.2
Mg12 <sup>b</sup>	8l	0	0.1687(5)	0.1095(5)	1.4

Atom	$B_{11} \times 10^4$	$B_{22} \times 10^4$	$B_{33} \times 10^4$	$B_{12} \times 10^4$	$B_{13} \times 10^4$	$B_{23} \times 10^4$
Zn1	21(1)	18(1)	16(1)	0	0	-2(1)
Zn2	15(1)	16(1)	22(1)	0(1)	0	0
Zn3	17(1)	32(1)	12(1)	0	0(1)	0
Zn4	33(2)	18(1)	28(2)	0	0	0
Zn5	23(1)	16(1)	21(1)	0	0	0
Zn6	19(2)	15(2)	11(2)	0	0	0
Zn7	26(2)	16(2)	18(2)	0	0	3(2)
Zn8	16(3)	19(3)	19(4)	0	0	-3(3)
Mg1	22(2)	14(1)	19(2)	-2(1)	0(2)	-2(2)
Mg2	21(2)	28(2)	18(2)	2(2)	3(2)	-1(2)
Mg3	22(2)	16(1)	19(2)	1(1)	-1(2)	2(2)
Mg4	8(2)	21(2)	10(2)	0	5(2)	0
Mg5	17(3)	19(2)	27(3)	0	6(2)	0
Mg6	7(2)	7(2)	6(2)	-5(2)	0	0
Mg7	36(3)	3(2)	3(2)	-2(2)	0	0
Mg8	17(4)	18(3)	20(4)	0	0	0
Mg9	18(4)	19(4)	20(4)	0	0	0
Mg10	20(4)	17(3)	17(4)	0	0	0
Mg11	2(4)	4(4)	5(4)	0	0	-1(3)
Mg12	22(3)	13(3)	16(3)	0	0	-2(3)

<sup>a</sup> The expression of the anisotropic temperature factor is  $\exp\{-(h^2B_{11} + K^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})\}$ .

<sup>b</sup> The occupancy factors of these sites are 0.46(2), 0.24(2), 0.52(2), and 0.74(2) for Zn7, Zn8, Mg11, and Mg12, respectively.

UNICS-III (9) on the FACOM 230-75 computer of this Institute.

As no marked differences between the intensities  $I_{hkl}$  and  $I_{\bar{h}\bar{k}\bar{l}}$  were observed, the centrosymmetric space group  $Immm$  was chosen. The positions of five Zn atoms (Zn1, 4–7) were determined from the examination of a Patterson map. Two Zn (Zn2, 3) and eleven Mg (Mg1–10, 12) were located by the iterative Fourier method. The least-squares refinement of this structure with isotropic temperature factors gave an  $R$  value ( $= \sum ||F_o| - |F_c|| / \sum |F_o|$ ) of 9.2%. However, the difference synthesis calculated at this stage showed strong minimum and maximum at Zn7 site (A site or hole A) and Mg12 (B site or hole B), respectively. Considering both the chemical composition and measured density of the crystal, as shown in Table I, each of the two holes was regarded as being statistically and almost fully occupied by Zn and Mg atoms. However, to estimate the approximate numbers of electrons of the two sites, assuming that these are fractionally occupied by Zn atoms alone, the structure was refined with the isotropic temperature factors ( $R = 6.8\%$ ). The occupancies obtained were 0.66 and 0.54 for the hole A and the hole B, respectively. This, in electron counting, corresponds to  $0.43\text{Zn}(\text{Zn7}) + 0.57\text{Mg}(\text{Mg11})$  for the hole A and  $0.23\text{Zn}(\text{Zn8}) + 0.77\text{Mg}(\text{Mg12})$  for the hole B. Starting from these values, the final least-squares refinement with the anisotropic temperature factors (119 independent parameters) was performed by repeating the following procedures twice. (1) The five cycle refinement of the structure including the occupancies of Zn7 (hole A) and Mg12 (hole B) with fixing those of Mg11 (hole A) and Zn8 (hole B). (2) The five cycle refinement of the structure including the occupancies of Mg11 (hole A) and Zn8 (hole B) with fixing those of Zn7 (hole A) and Mg12 (hole B). The  $R$  value reduced to 4.8%. The occupancies

thus obtained were  $0.46(2)\text{Zn7} + 0.52(2)\text{Mg11}$  for the hole A and  $0.24(2)\text{Zn8} + 0.74(2)\text{Mg12}$  for the hole B. The difference synthesis calculated at the final stage showed no more maxima or minima exceeding 3% of Mg maximum in the  $F_o$ -synthesis. The atomic coordinates and temperature factors are given in Table II, and the observed and calculated structure factors are compared in a separate table.<sup>1</sup> The unusually low temperature factor ( $B_{\text{av.}} = 0.2 \text{ \AA}^2$ ) obtained for Mg11 may be due to its low occupancy which makes the refinement insensitive especially to the temperature factor.

### Description of the Structure and Discussion

The distances between neighboring atoms are presented in Table III. As seen from the table, the distances between Zn atoms ranging from 2.71 to 3.07 Å are appreciably shorter than most of the Mg–Mg distances, 2.82, 3.00–3.35, 3.65 Å. This is consistent with the case in  $\text{MgZn}_2$  (10); the Zn–Zn and Mg–Mg distances observed for this compound are 2.54, 2.62, or 2.64 Å and 3.17 or 3.20 Å, respectively. In the present crystal, the Zn–Mg distances, 2.60–3.20 Å, are somewhat scattered as compared with the Zn–Zn and Mg–Mg distances. On the whole, they are slightly longer than the Zn–Zn distances and shorter than the Mg–Mg distances. A similar tendency is seen among the three kinds of interatomic distances observed for

<sup>1</sup> See NAPS document No. 03697 for 12 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche publications, P.O. Box 3513, Grand Central Station, New York, New York 10163. Remit in advance for each NAPS Accession number. Institutions and organizations may use purchase orders when ordering, however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are \$5.00. Microfiche are \$3.00. Outside of the U.S. and Canada, postage is \$3.00 for a photocopy or \$1.50 for a fiche.

TABLE III  
INTERATOMIC DISTANCES<sup>a</sup>

Zn1–Zn4 <sup>o</sup>	2.712(3)	Zn8–Mg9 <sup>o</sup>	3.06(1)	Mg5–Mg5 <sup>l</sup>	3.089(8)
–Zn7 <sup>o</sup>	2.715(5)	–Mg12 <sup>o</sup>	0.02(1) <sup>o</sup>	–Mg5 <sup>x</sup>	3.346(8)
–Zn8 <sup>o</sup>	2.802(7)	–Mg12 <sup>x</sup>	3.07(1)	–2Mg7 <sup>iii,xlv</sup>	3.649(7)
–2Mg1 <sup>o,i</sup>	3.107(4)	Mg1–Zn1 <sup>o</sup>	3.107(4)	–2Mg9 <sup>o,vii</sup>	3.126(7)
–2Mg2 <sup>o,i</sup>	2.952(4)	–Zn2 <sup>o</sup>	3.196(4)	Mg6–Zn2 <sup>iii</sup>	2.733(5)
–2Mg3 <sup>o,i</sup>	3.117(4)	–Zn3 <sup>o</sup>	2.961(3)	–Zn6 <sup>o</sup>	2.945(4)
–2Mg5 <sup>o,i</sup>	3.055(4)	–Zn5 <sup>o</sup>	3.138(3)	–2Zn8 <sup>o,x</sup>	3.123(6)
–Mg9 <sup>o</sup>	2.905(2)	–Zn7 <sup>o</sup>	3.032(5)	–2Mg2 <sup>o,x</sup>	3.107(6)
–Mg11 <sup>o</sup>	2.729(8)	–Zn8 <sup>o</sup>	3.182(7)	–2Mg3 <sup>iii,xv</sup>	3.195(4)
–Mg12 <sup>o</sup>	2.817(7)	–Mg1 <sup>l</sup>	3.143(5)	–2Mg4 <sup>o,x</sup>	3.031(5)
Zn2–Zn5 <sup>o</sup>	2.818(2)	–Mg2 <sup>o</sup>	3.198(5)	–Mg6 <sup>v</sup>	2.981(6)
–2Zn <sup>o,ii</sup>	2.769(3)	–Mg2 <sup>iii</sup>	3.141(5)	–Mg10 <sup>iii</sup>	3.248(8)
–2Mg1 <sup>o,ii</sup>	3.196(4)	–Mg3 <sup>o</sup>	3.252(5)	–Mg12 <sup>o,x</sup>	3.117(6)
–2Mg2 <sup>iii,iv</sup>	2.940(4)	–Mg3 <sup>iii</sup>	3.382(5)	Mg7–Zn2 <sup>o</sup>	2.762(3)
–2Mg3 <sup>o,ii</sup>	3.078(4)	–Mg4 <sup>o</sup>	3.224(4)	–Mg10 <sup>o,ii</sup>	2.762(3)
–Mg6 <sup>iii</sup>	2.733(5)	–Mg7 <sup>o</sup>	3.138(5)	–Zn5 <sup>o</sup>	2.799(6)
–Mg7 <sup>o</sup>	2.762(3)	–Mg8 <sup>o</sup>	3.250(4)	–2Mg1 <sup>o,ii</sup>	3.138(5)
–Mg10 <sup>o</sup>	3.158(3)	–Mg11 <sup>o</sup>	3.155(8)	–2Mg2 <sup>iii,iv</sup>	3.047(6)
–2Mg11 <sup>o,ii</sup>	2.807(5)	–Mg12 <sup>o</sup>	3.184(7)	–2Mg5 <sup>iii,iv</sup>	3.649(7)
Zn3–2Mg1 <sup>o,v</sup>	2.961(3)	Mg2–Zn1 <sup>o</sup>	2.952(4)	–Mg7 <sup>v</sup>	2.824(6)
–2Mg2 <sup>iii,vi</sup>	3.573(4)	–Zn2 <sup>iii</sup>	2.940(4)	–2Mg8 <sup>o,ii</sup>	3.354(6)
–2Mg3 <sup>iii,vi</sup>	2.932(4)	–Zn8 <sup>o</sup>	3.052(5)	Mg8–2Zn3 <sup>o,i</sup>	2.986(3)
–Mg4 <sup>o</sup>	2.629(5)	–Mg2 <sup>x</sup>	3.300(5)	–2Zn5 <sup>o,v</sup>	2.981(5)
–Mg5 <sup>iii</sup>	2.691(6)	–Mg3 <sup>o</sup>	3.130(5)	–4Mg1 <sup>o,i,v,xvi</sup>	3.250(4)
–2Mg7 <sup>o,v</sup>	2.762(3)	–Mg3 <sup>iii</sup>	3.260(5)	–2Mg4 <sup>o,i</sup>	3.328(9)
–Mg8 <sup>o</sup>	2.986(3)	–Mg5 <sup>o</sup>	3.281(4)	–4Mg7 <sup>o,i,v,xvi</sup>	3.354(6)
Zn4–2Zn1 <sup>o,vii</sup>	2.712(3)	–Mg6 <sup>o</sup>	3.107(6)	–Mg8 <sup>ii</sup>	3.23(1)
–2Zn7 <sup>o,vii</sup>	2.731(4)	–Mg7 <sup>iii</sup>	3.047(6)	Mg9–2Zn1 <sup>o,x</sup>	2.905(2)
–4Mg3 <sup>o,i,vii,xviii</sup>	3.137(4)	–Mg9 <sup>o</sup>	3.196(5)	–2Zn8 <sup>o,x</sup>	3.06(1)
–2Mg5 <sup>o,i</sup>	3.029(6)	–Mg12 <sup>o</sup>	3.060(5)	–4Mg2 <sup>o,i,x,xvii</sup>	3.196(5)
–2Mg10 <sup>o,i</sup>	3.176(5)	Mg3–Zn1 <sup>o</sup>	3.117(4)	–4Mg5 <sup>o,i,x,xvii</sup>	3.126(7)
–2Mg11 <sup>o,vii</sup>	2.601(8)	–Zn2 <sup>o</sup>	3.078(4)	–2Mg12 <sup>o,x</sup>	3.07(1)
Zn5–2Zn2 <sup>o,i</sup>	2.818(2)	–Zn3 <sup>iii</sup>	2.932(4)	Mg10–2Zn2 <sup>o,vii</sup>	3.158(3)
–2Zn7 <sup>o,ii</sup>	2.740(5)	–Zn4 <sup>o</sup>	3.137(4)	–2Zn4 <sup>o,ii</sup>	3.176(5)
–4Mg1 <sup>o,i,ii,ix</sup>	3.138(4)	–Zn7 <sup>o</sup>	3.093(4)	–4Zn7 <sup>o,ii,vii,xviii</sup>	3.202(5)
–2Mg7 <sup>o,i</sup>	2.799(6)	–Mg1 <sup>o</sup>	3.252(5)	–4Mg3 <sup>o,ii,vii,xviii</sup>	3.268(5)
–2Mg8 <sup>o,ii</sup>	2.981(5)	–Mg1 <sup>iii</sup>	3.382(5)	–2Mg6 <sup>iii,xiv</sup>	3.248(8)
–2Mg11 <sup>o,ii</sup>	2.870(8)	–Mg2 <sup>o</sup>	3.130(5)	–Mg10 <sup>o</sup>	3.23(1)
Zn6–4Zn8 <sup>o,v,x,xi</sup>	2.901(7)	–Mg2 <sup>iii</sup>	3.260(5)	–4Mg11 <sup>o,ii,vii,xviii</sup>	3.081(8)
–4Mg4 <sup>o,i,x,xii</sup>	2.865(5)	–Mg3 <sup>vi</sup>	3.148(5)	Mg11–Zn1 <sup>o</sup>	2.729(8)
–4Mg6 <sup>o,i,v,xiii</sup>	2.945(4)	–Mg4 <sup>iii</sup>	3.241(5)	–2Zn2 <sup>o,i</sup>	2.807(5)
–4Mg12 <sup>o,v,x,xi</sup>	2.887(7)	–Mg5 <sup>o</sup>	3.332(6)	–Zn4 <sup>o</sup>	2.601(8)
Zn7–Zn1 <sup>o</sup>	2.715(5)	–Mg6 <sup>ii</sup>	3.195(4)	–Zn5 <sup>o</sup>	2.870(8)
–2Zn2 <sup>o,i</sup>	2.769(3)	–Mg10 <sup>o</sup>	3.268(5)	–Zn7 <sup>o</sup>	0.158(9) <sup>o</sup>
–Zn4 <sup>o</sup>	2.731(4)	–Mg11 <sup>o</sup>	3.061(5)	–Zn7 <sup>ii</sup>	2.791(9)
–Zn5 <sup>o</sup>	2.740(5)	Mg4–Zn3 <sup>o</sup>	2.629(5)	–2Mg1 <sup>o,i</sup>	3.155(8)
–Zn7 <sup>ii</sup>	2.799(6) <sup>o</sup>	–Zn6 <sup>o</sup>	2.865(5)	–2Mg3 <sup>o,i</sup>	3.061(5)
–2Mg1 <sup>o,i</sup>	3.032(5)	–2Zn8 <sup>o,v</sup>	3.018(7)	–2Mg10 <sup>o,i</sup>	3.081(8)
–2Mg3 <sup>o,i</sup>	3.093(4)	–2Mg1 <sup>o,v</sup>	3.224(4)	–Mg11 <sup>ii</sup>	2.77(1) <sup>o</sup>
–2Mg10 <sup>o,i</sup>	3.202(5)	–2Mg3 <sup>iii,vi</sup>	3.241(5)	Mg12–Zn1 <sup>o</sup>	2.817(7)
–Mg11 <sup>o</sup>	0.158(9) <sup>o</sup>	–Mg4 <sup>i</sup>	3.009(6)	–Zn6 <sup>o</sup>	2.887(7)
–Mg11 <sup>ii</sup>	2.791(9)	–2Mg6 <sup>o,v</sup>	3.031(5)	–Zn8 <sup>o</sup>	0.02(1) <sup>o</sup>
Zn8–Zn1 <sup>o</sup>	2.802(7)	–Mg8 <sup>o</sup>	3.328(9)	–Zn8 <sup>x</sup>	3.07(1)
–Zn6 <sup>o</sup>	2.901(7)	–2Mg12 <sup>o,v</sup>	3.005(7)	–2Mg1 <sup>o,i</sup>	3.184(7)
–Zn8 <sup>x</sup>	3.07(1)	Mg5–2Zn1 <sup>o,vii</sup>	3.055(4)	–2Mg2 <sup>o,i</sup>	3.060(5)
–2Mg1 <sup>o,i</sup>	3.182(7)	–Zn3 <sup>iii</sup>	2.6911(6)	–2Mg4 <sup>o,i</sup>	3.005(7)
–2Mg2 <sup>o,i</sup>	3.052(5)	–Zn4 <sup>o</sup>	3.029(6)	–2Mg6 <sup>o,i</sup>	3.117(6)
–2Mg4 <sup>o,i</sup>	3.018(7)	–2Mg2 <sup>o,vii</sup>	3.281(4)	–Mg9 <sup>o</sup>	3.07(1)
–2Mg6 <sup>o,i</sup>	3.123(6)	–2Mg3 <sup>o,vii</sup>	3.332(6)	–Mg12 <sup>x</sup>	3.07(1)

<sup>a</sup> The distances between every atomic site and sites surrounding it are listed. The atomic sites are designated by the following symmetry codes: none or  $o(x, y, z)$ ,  $i(-x, y, z)$ ,  $ii(x, y, -z + 1)$ ,  $iii(-x + 1/2, -y + 1/2, -z + 1/2)$ ,  $iv(-x + 1/2, -y + 1/2, z + 1/2)$ ,  $v(x, -y, z)$ ,  $vi(-x + 1/2, -y - 1/2, -z + 1/2)$ ,  $vii(x, -y + 1, z)$ ,  $viii(-x, -y + 1, z)$ ,  $ix(-x, y, -z + 1)$ ,  $x(x, y, -z)$ ,  $xi(x, -y, -z)$ ,  $xii(-x, y, -z)$ ,  $xiii(-x, -y, z)$ ,  $xiv(-x + 1/2, y + 1/2, -x + 1/2)$ ,  $xv(-x + 1/2, -y + 1/2, z - 1/2)$ ,  $xvi(-x, -y, z)$ ,  $xvii(-x, y, -z)$ , and  $xviii(x, -y + 1, -z + 1)$ .

<sup>b</sup> Distances between the sites. See the text.

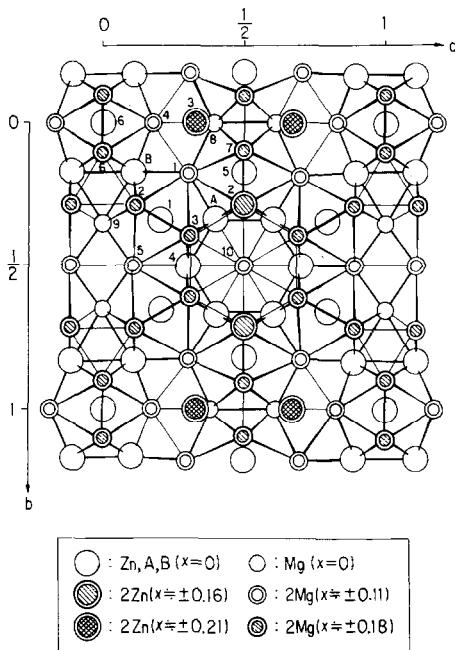


FIG. 1. The structure in the region of  $-0.25 < x < 0.25$  as seen along the  $a$  axis, showing an arrangement of icosahedral coordination polyhedra.

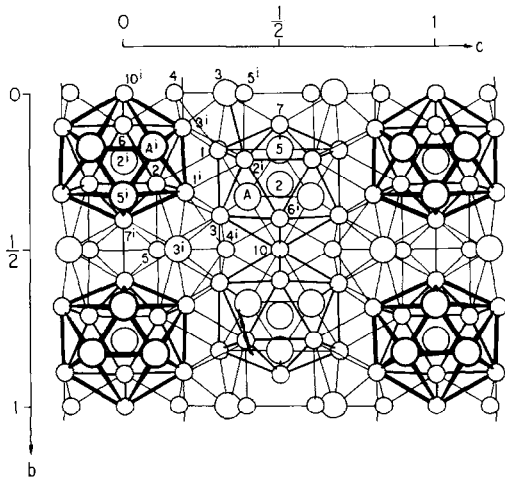


FIG. 2. The structure in the region of  $0.05 < x < 0.45$  including Zn5( $x = 0, 1/2$ ) and B( $x = 0, 1/2$ ) sites as seen along the  $a$  axis, showing an arrangement of icosahedral coordination polyhedra. The large circle represents Zn, A, or B site, and the small circle Mg site. The sites within  $0 \leq y \leq 0.5, 0 \leq z \leq 0.5$  are marked with the symmetry codes; none ( $x, y, z$ ),  $i(-x + 1/2, -y + 1/2, -z + 1/2)$ .

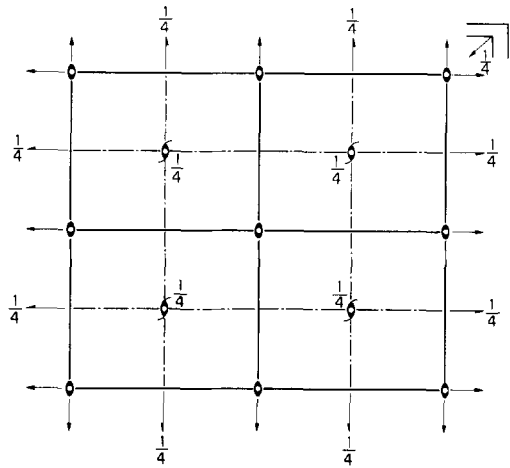


FIG. 3. The symmetry of the space group  $Im\bar{m}m$ .

$MgZn_2$ . (The Zn–Mg distance in  $MgZn_2$  is 3.04 Å.) The Zn8 and Mg12 sites located in the hole B are almost coincident (Table II or Zn8–Mg12 distance in Table III). On the other hand, Zn7 and Mg11 sites in the hole A are slightly shifted from each other (Table II); the distance of the sites is 0.14 Å (Zn7–Mg11 distance in Table III). The distance between Mg11(A) and Mg11<sup>ii</sup>(A<sup>ii</sup>), 2.77 Å, is noticeably shorter than every

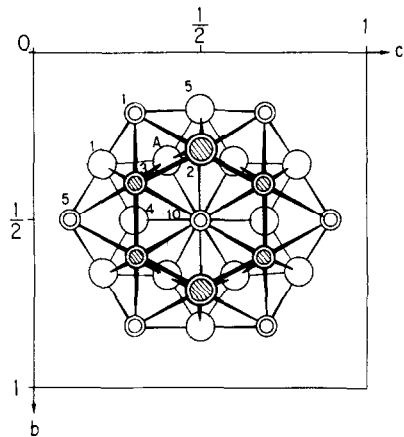


FIG. 4. The structure in the region of  $-0.25 < x < 0.25$  around  $bc$  face center as seen along the  $a$  axis, showing the interpenetration of icosahedral coordination polyhedra. The circles representing atomic sites are the same as those used in Fig. 1.

TABLE IV  
INTERPENETRATION OR LINKAGES BETWEEN ICOSAHEDRAL COORDINATION POLYHEDRA<sup>a</sup>

Icosahedron	Interpenetrating icosahedron	Icosahedron sharing		
		Triangular face	Edge	Apex
Zn1	Zn4, A	Zn1 <sup>ii</sup> , Zn2, Zn2 <sup>iii</sup> , Zn5		Zn1 <sup>viii</sup> , Zn2 <sup>ix</sup> , Zn2 <sup>x</sup> , Zn6, A <sup>iv</sup> , A <sup>ii</sup>
Zn2	Zn5, A, A <sup>i</sup>	Zn1, Zn1 <sup>iv</sup> , Zn2 <sup>iii</sup> , Zn4, Zn4 <sup>iv</sup>		Zn1 <sup>ix</sup> , Zn1 <sup>xi</sup> , Zn <sup>ii</sup> , Zn6 <sup>xii</sup>
Zn4	Zn1, Zn1 <sup>ii</sup> , A, A <sup>ii</sup>	Zn2, Zn2 <sup>iii</sup> , Zn2 <sup>ii</sup> , Zn2 <sup>v</sup> , A <sup>iv</sup> , A <sup>vi</sup>	Zn4 <sup>iv</sup>	Zn5, Zn5 <sup>ii</sup>
Zn5	Zn2, Zn2 <sup>iii</sup> , A, A <sup>iv</sup>	Zn1, Zn1 <sup>iv</sup>	Zn5 <sup>vii</sup>	Zn4, Zn4 <sup>iv</sup>
Zn6				Zn1, Zn1 <sup>vii</sup> , Zn1 <sup>viii</sup> , Zn1 <sup>xiii</sup> , Zn2 <sup>ix</sup> , Zn2 <sup>x</sup> , Zn2 <sup>xiv</sup> , Zn2 <sup>xv</sup>
A (Zn7, Mg11)	Zn1, Zn2, Zn2 <sup>iii</sup> , Zn4, Zn5, A <sup>iv</sup>	Zn4 <sup>iv</sup> , A <sup>ii</sup>		Zn1 <sup>iv</sup> , Zn1 <sup>ii</sup>

<sup>a</sup> The polyhedra are represented by the center atoms designated by the following symmetry codes: none( $x, y, z$ ), i( $x, y, -z + 1$ ), ii( $x, -y + 1, z$ ), iii( $-x, y, z$ ), iv( $x, y, -z + 1$ ), v( $-x, -y + 1, z$ ), vi( $x, -y + 1, -z + 1$ ), vii( $x, -y, z$ ), viii( $x, y, -z$ ), ix( $-x + 1/2, -y + 1/2, -z + 1/2$ ), x( $x - 1/2, -y + 1/2, -z + 1/2$ ), xi( $-x + 1/2, -y + 1/2, z + 1/2$ ), xii( $x + 1/2, y + 1/2, z + 1/2$ ), xiii( $x, -y, -z$ ), xiv( $-x + 1/2, y - 1/2, -z + 1/2$ ), and xv( $x - 1/2, y - 1/2, -z + 1/2$ ).

another Mg–Mg distance. So, the simultaneous occupation of the adjacent Mg11(A) and Mg11(A<sup>ii</sup>) positions by Mg atoms never seems to take place. Whereas, as can be acknowledged from comparison with other Zn–Mg distances, the Zn7(A)–Mg11(A<sup>ii</sup>) distance, 2.79 Å, is a reasonable one for a Zn–Mg bond length. This means that simultaneous occupation of the two adjacent positions by the different atoms is permissible. Thus, it is inferred that the Zn7(A)–Mg11(A<sup>ii</sup>) or Mg11(A)–Zn7<sup>ii</sup>(A<sup>ii</sup>) pairs are distributed statistically over the whole crystal, because the hole A is almost fully occupied by Zn and Mg atoms with approximately equal occupancies.

The structure of Zn<sub>20</sub>Mg<sub>51</sub> is conveniently described as an arrangement of distorted icosahedral coordination polyhedra. All the atomic sites except Zn3 belong to

this arrangement; the Zn3 site is located in the hole outside the icosahedra. Figure 1 shows the structure between  $x = -0.25$  and  $x = +0.25$ , and Fig. 2 shows that between  $x = 0.05$  and  $x = 0.45$  including the A site ( $x = 0, 1/2$ ) and Zn5 site ( $x = 0, 1/2$ ). Every Zn site other than Zn3 and Zn8(B) is located at the center of an icosahedron. As for the Mg sites, only Mg11(A) is located at the center of an icosahedron. The icosahedron centered at Zn2 (Fig. 2), and the rests (Fig. 1) are oriented so as to have its one of the pseudo  $\bar{3}$  and twofold axes almost parallel to the  $a$  axis, respectively. Except for the one centered at (0,0,0), the icosahedra are interpenetrated with their first neighbors, sharing triangular faces with the second neighbors. Two of these icosahedra are sharing their respective one edge with their third neighbors and apexes with the fourth

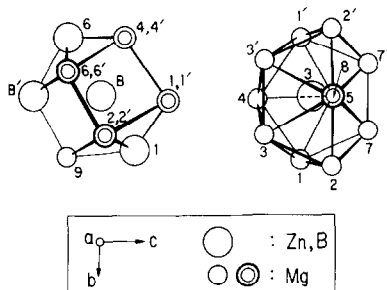


FIG. 5 The natures of the coordinations of B(Zn8, Mg11) and Zn3 sites as seen along the  $a$  axis.

neighbors, and the remaining ones sharing apexes with their third neighbors. The icosahedron centered at the origin is linked to its eight first neighbors by sharing its apexes. The spatial interrelations of the icosahedra are outlined in Table IV, where each icosahedron is represented by its center atom. The modes of the interpenetration or combination among the icosahedra can

be seen from Fig. 1 and Fig. 2 with the aid of the space group symmetry (Fig. 3); the interpenetrations around the center of Fig. 1 are thoroughly drawn in Fig. 4. Figure 5 shows the natures of the coordinations of the B site (Zn8, Mg12) and Zn3 site. The B site is located at the center of the pentagonal prism with polar atoms. The Zn3 site is lying in an irregular polyhedron outside any of the icosahedra and is made up of 18 triangular faces. The natures of the coordinations of the Mg sites other than those in the hole A and the hole B are shown in Fig. 6. As seen from the figure, Mg2, Mg4, Mg6, and Mg9 sites center the pentagonal prisms with polar atoms. But the sequence of the apical atoms of each of the polyhedra is different from every other one. The other sites are lying at the centers of the various irregular polyhedra having numerous triangular planes and one or a few distorted square planes; the coordination polyhedra of Mg1, Mg3, and Mg5 sites have 3 square planes and 18 triangular planes; the polyhedron centered by Mg8 site has 2 square planes and 18 triangular planes, and that centered by Mg10 site has 2 square planes and 22 triangular planes; the Mg7 site centers a polyhedron having one square plane and 20 triangular planes, which can be derived from a combination of a pentagonal and a hexagonal pyramid. In Table V, the coordination numbers and coordinating atoms are given for every atomic site in the crystal. Average coordination numbers about Zn and Mg atoms are 11.8 and 13.1, respectively. It has been found in our study (11) of the amorphous state of this composition that the average coordination number of the amorphous state was 12 and average interatomic distance was 3.0 Å. It is interesting to note that the structure of the amorphous state is close to that of the crystallized state. The asymmetric unit obtained from the final structure data including occupational parameters (Table II) is  $\text{Mg}_{6.38(2)}\text{Zn}_{2.48(2)}$ . The good agreements be-

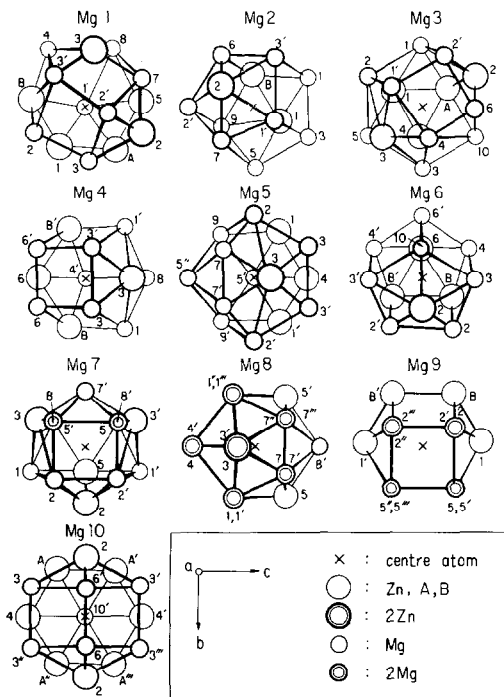


FIG. 6. The natures of the coordinations of Mg sites as seen along the  $a$  axis.



TABLE V  
THE COORDINATION NUMBER AND COORDINATING  
ATOMS ABOUT THE ATOMIC SITES<sup>a</sup>

Atom	coordination number	Coordinating	
		Atoms	(Atoms) <sub>av.</sub>
Zn1	12	Zn, A, B, 9Mg	1.7Zn, 10.2Mg
Zn2	12	Zn, 2A, 9Mg	1.9Zn, 10Mg
Zn3	11	11Mg	
Zn4	12	2Zn, 2A, 8Mg	2.9Zn, 9Mg
Zn5	12	2Zn, 2A, 8Mg	2.9Zn, 9Mg
Zn6	12	4B, 8Mg	Zn, 10.9Mg
Mg1	14	4Zn, A, B, 8Mg	4.7Zn, 9.2Mg
Mg2	12	2Zn, B, 9Mg	2.2Zn, 9.7Mg
Mg3	14	4Zn, A, 9Mg	4.5Zn, 9.5Mg
Mg4	12	2Zn, 2B, 8Mg	2.5Zn, 9.5Mg
Mg5	14	4Zn, 10Mg	
Mg6	12	2Zn, 2B, 8Mg	2.5Zn, 9.5Mg
Mg7	13	4Zn, 9Mg	
Mg8	15	4Zn, 11Mg	
Mg9	12	2Zn, 2B, 8Mg	2.5Zn, 9.5Mg
Mg10	15	4Zn, 4A, 7Mg	5.8Zn, 9.0Mg
A	12	5Zn, A, 6Mg	5.5Zn, 6.5Mg
B	12	2Zn, B, 9Mg	2.2Zn, 9.7Mg

<sup>a</sup> For those coordinated with A or B site, the numbers of coordinating atoms averaged over the whole crystal are presented.

tween the atomic ratio determined by X-ray and that by chemical analyses and between the density determined by the X-ray and that by the Archimedes method (Table I) prove the validity of the present assignment of atomic sites. Therefore, the composition  $Mg_{51}Zn_{20}$ , obtained with multiplying the asymmetric unit by 8, is suggested as a chemical unit of this crystal phase; the

composition differs a little from " $Mg_7Zn_3$ " ( $Mg_{47}Zn_{20}$ ) as described in reference books.

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