

## Crystal Structure of a New Stacking Variant of a Friauf–Laves Phase in the System Mg–Cu–Ni

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The crystal structure of a pseudo-binary Friauf–Laves phase compound  $\text{MgNi}_{2-55}$  mol%  $\text{MgCu}_2$  has been determined by the X-ray diffraction method. The structure is hexagonal and has a new stacking sequence which is represented as  $ABC'A'C'B'$  consisting of six fundamental composite layers of Friauf–Laves phases. The space group is  $P6_3/mmc$ , with the unit-cell dimensions,  $a = 4.917 \pm 0.001$ ,  $c = 24.040 \pm 0.003$  Å,  $c/a = 4.889$ . There are 12 formula units,  $\text{Mg}(\text{Ni}_{0.45}\text{Cu}_{0.55})_2$ , per unit cell. The atomic parameters were refined by the full-matrix least-squares method allowing for isotropic thermal vibrations. The final  $R$  value for 180 structure amplitudes was 0.114. The amounts of shift of the atomic parameters after the refinement were very small compared with the trial structure. It was found that the kinds of coordination polyhedra surrounding each atom were the same as those in Friauf–Laves phases, *i.e.* icosahedron [CN(12)] and Friauf-polyhedron [CN(16)]. These polyhedra are connected to form a chain along [001] in the order CN(12)–CN(16)–CN(16)–CN(12)–CN(16)–CN(16)–CN(12).

### Introduction

Friauf–Laves phases, which are known as size factor compounds, are classified into the following three closely related fundamental structures: cubic  $C_{15}$  ( $\text{MgCu}_2$ ) structure, hexagonal  $C_{14}$  ( $\text{MgZn}_2$ ) and  $C_{36}$  ( $\text{MgNi}_2$ ) structures. Besides the atomic radius ratio, the electron concentration is generally important in relation to the interaction between the Fermi surface and Brillouin zone boundaries. Laves & Witte (1936) investigated alloys of Mg-base ternary Friauf–Laves phases to see the effect due to the change of electron concentration, and found that the replacement of Cu in  $\text{MgCu}_2$  by a metal of higher valency, such as Zn, Al or Si, resulted in the change of the cubic  $C_{15}$  type into the hexagonal  $C_{36}$  or  $C_{14}$  type, depending upon the electron:atom ratio ( $e/a$ ). Lieser & Witte (1952) studied the ternary systems of Mg–Cu–Zn,

Mg–Ni–Zn and Mg–Cu–Ni in detail, and found a close relationship between electron concentration and crystal structure, such that the phase boundaries of  $C_{14}$ ,  $C_{15}$  and  $C_{36}$  appear at nearly the same values of  $e/a$  for all the alloys under consideration.

Komura, Mitarai, Nakatani, Iba & Shimizu (1970) repeated the investigation on the pseudo-binary systems of  $\text{MgZn}_2$ – $\text{MgCu}_2$  and  $\text{MgZn}_2$ – $\text{MgAg}_2$ , and confirmed the fact that the crystal structures of these systems were strongly governed by the electron concentration. In addition, three new stacking variants were found between the homogeneity ranges of  $C_{14}$  and  $C_{36}$  type structures. These three stacking variants were called 8-, 9- and 10-layer types according to their layer stacking. As to the pseudo-binary  $\text{MgCu}_2$ – $\text{MgNi}_2$  system, on the other hand, a phase diagram had been given by Lieser & Witte (Fig. 1) in which two phases are mixed in the range of 40 to 60 mol% of  $\text{MgCu}_2$ . A reinvestigation of the  $\text{MgCu}_2$ – $\text{MgNi}_2$  system was undertaken in the course of the study of Mg-base ternary Friauf–Laves phases, and contrary to their results, a new phase was found in the vicinity of 50 to 55 mol% of  $\text{MgCu}_2$  from the powder diffraction pattern of X-rays. The purpose of the present investigation was to determine this structure and its relation to the neighbouring region of the phase diagram.

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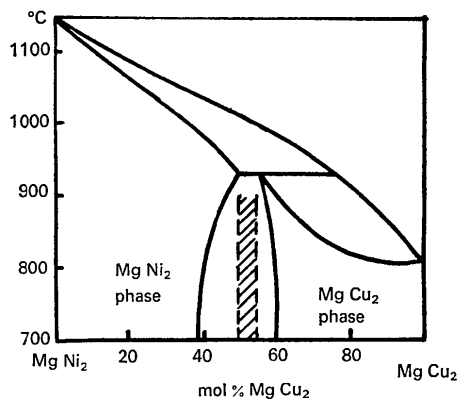


Fig. 1. Phase diagram of pseudo-binary system of  $\text{MgNi}_{2-x}$  mol%  $\text{MgCu}_2$  (after Lieser & Witte, 1952).

### Experimental

#### Sample preparation

A series of pseudo-binary  $\text{MgNi}_{2-x}$  mol%  $\text{MgCu}_2$  alloys were prepared by melting pieces of pure copper and magnesium together with nickel powder in a graphite crucible by induction heating in an argon gas atmosphere. All materials used were above the grade of 99.9% in purity. The melt was vigorously stirred and then cast into a cylindrical graphite mould. The alloys thus obtained were annealed at varying temper-

atures between 500 and 800°C in a small graphite crucible inside an argon-filled sealed silica tube. For the single-phase regions of  $C_{36}$  and  $C_{15}$  the result of Lieser & Witte was confirmed by X-ray diffractometer measurements on powder samples of various compositions. However, it was noted that the relative intensities for the samples of 50 to 55%  $MgCu_2$  could not be interpreted as a mixture of  $C_{15}$  and  $C_{36}$  types. In addition, a few extra reflexions were found besides those of  $C_{15}$  and  $C_{36}$ . These facts indicated the presence of a new modification in this range. Thus, tiny single crystals of irregular shapes with a linear dimension of about  $50\mu$  were picked up from the crushed fragments of the alloy of 55%  $MgCu_2$ . Single-crystal work has been done mainly on the specimens of this composition. The alloy used for single-crystal work was chemically analysed and the composition thus determined [Cu, 47.3%; Ni, 35.3%; Mg, the rest (17.4%)] was found to be very close to the prepared composition (Cu, 47.5%; Ni, 35.9%; Mg, 16.6%).

#### Unit cell and space group

Laue, oscillation and Weissenberg photographs of the layer lines 0 to 2 about the [010] axis were taken with Cu  $K\alpha$  radiation. The crystals showed that the structure was hexagonal, having Laue symmetry  $6/mmm$ . Systematic absence of the reflexions  $hhl$  and  $00l$  for  $l \neq 6n$  indicated the probable space groups  $P6_2c$ ,  $P6_3mc$  or  $P6_3/mmc$ .

The identity period of the  $c$  axis is different from those of  $MgCu_2$  and  $MgNi_2$  and is approximately  $\frac{6}{4}$  times that of  $MgNi_2$ . Since  $MgNi_2$  is with the 4-layer structure with respect to the layer stacking (Komura *et al.*, 1970), the phase in question should possess a 6-layer structure. Accurate lattice constants were measured from Weissenberg photographs on which diffraction patterns of Si powder were recorded as a standard. The Cu  $K\alpha$  and Cu  $K\beta$  radiations ( $\lambda_{\alpha 1} =$

$1.54051 \text{ \AA}$ ,  $\lambda_{\alpha 2} = 1.54433 \text{ \AA}$ ,  $\lambda_{\beta} = 1.39217 \text{ \AA}$ ) were used. The unit-cell dimensions were determined using the Nelson-Riley extrapolation, as follows:  $a = 4.917 \pm 0.001 \text{ \AA}$ ,  $c = 24.040 \pm 0.003 \text{ \AA}$   $c/a = 4.889$  for a  $MgNi_2$ -55%  $MgCu_2$  sample.

Intensities of reflexions were estimated visually by the use of a calibrated intensity scale. Powder diffrac-

Table 1. Powder-diffraction data for  $MgNi_2$ -55 mol%  $MgCu_2$

$h$	$k$	$l$	$d_{obs}$	$d_{cal}$	$I_{obs}$	$I_{cal}$
1	0	1	4.2028 Å	4.19298 Å	20	40.92
1	0	2	—	{4.01382	—	{72.61
0	0	6	4.0198	{4.00667	48	{63.67
1	0	3	3.7717	3.76031	7	23.06
1	0	5	—	3.18777	—	1.71
1	0	7	—	2.67323	—	0.09
1	1	0	—	{2.45850	—	{15.14
1	0	8	2.4618	{2.45522	7	{8.61
1	0	9	2.2656	2.26278	14	48.15
2	0	1	2.1212	2.12082	6	6.79
2	0	2	—	{2.09649	—	{28.05
1	1	6	2.0967	{2.09547	83	{100.00
1	0	10	—	{2.09343	—	{60.57
2	0	3	2.0581	2.05773	34	57.93
2	0	4	2.0064	2.00691	34	67.83
0	0	12	2.0029	2.00333	39	32.57
2	0	5	—	{1.94679	—	{22.15
1	0	11	1.9463	{1.94434	12	{14.96
2	0	7	1.8099	1.80958	10	16.53
2	0	8	1.7369	1.73726	10	24.74
1	0	13	1.6962	1.69619	2	5.54
2	0	9	1.6653	1.66493	3	15.93
2	1	1	1.6055	1.60587	2	5.60
2	1	2	—	{1.59523	—	{7.36
2	0	10	1.5935	{1.59388	3	{4.28
1	0	14	—	{1.59254	—	{5.12
2	1	3	—	1.57796	—	0.50
2	0	11	—	1.52505	—	0.41
1	0	15	—	1.49995	—	0.44
3	0	0	—	{1.41942	—	{1.69
2	1	8	1.4186	{1.41879	1	{2.62
1	0	16	—	{1.41689	—	{1.05
2	0	13	—	1.39615	—	1.21
2	1	9	1.3781	1.37856	3	8.19
1	0	17	—	1.34205	—	1.03
3	0	6	—	{1.33794	—	{18.57
2	1	10	1.3369	{1.33741	17	{11.12
2	0	14	—	1.33662	—	5.75
0	0	18	—	1.33556	—	5.17
2	1	11	—	1.29596	—	4.52
2	0	15	1.2804	1.28045	2	14.90
2	2	0	1.2289	1.22925	9	21.08
2	0	16	1.2265	1.22761	7	15.60
2	1	13	—	1.21405	—	2.15
1	0	19	—	1.21286	—	0.07
3	1	1	—	1.17960	—	0.96
2	0	17	1.1776	1.17797	2	5.14
3	1	2	—	1.17537	—	1.49
2	2	6	—	1.17519	—	4.11
2	1	14	—	{1.17429	—	{1.94
1	1	18	1.1737	{1.17357	3	{4.50
1	0	21	—	1.10551	—	1.39
3	1	8	—	1.09918	—	0.72
2	0	19	—	1.08770	—	4.37
3	1	9	—	1.08016	—	3.70
4	0	1	—	1.06352	—	0.47
4	0	2	—	{1.06041	—	{1.72
3	1	10	1.0596	{1.06002	4	{4.61
1	0	22	—	{1.05843	—	{2.65

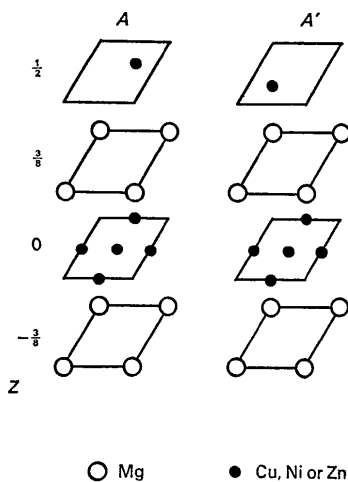


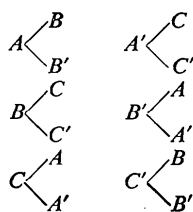
Fig. 2. Two kinds of composite layers,  $A$  and  $A'$ , of the Friauf-Laves phases. The parameter  $z$  is taken as a fraction of the distance between two kagomé nets.

tion data of spacings for  $\text{MgNi}_2$ -55%  $\text{MgCu}_2$  are listed in Table 1 together with  $I_{\text{obs}}$  and  $I_{\text{cal}}$  calculated from the refined structure described later.

### The trial structure

Three Friauf-Laves phase structures can be regarded as a stacking of six kinds of composite layers, each of which is constructed by one kagomé and three triangular nets (Komura, 1962). Two kinds of layers, called  $A$  and  $A'$ , are shown in Fig. 2 as examples. These differ from each other in the location of the triangular net placed at  $z = \frac{1}{2}$ . If  $A$  and  $A'$  are shifted  $\frac{1}{3}$  or  $\frac{2}{3}$  in the  $[\bar{1}10]$  direction of the hexagonal cell, one obtains  $B$  and  $B'$ , or  $C$  and  $C'$  layers respectively. Thus, the  $C_{14}$  ( $\text{MgZn}_2$ ) can be described as  $AB'$ , the  $C_{15}$  ( $\text{MgCu}_2$ ) as  $ABC$ , and the  $C_{36}$  ( $\text{MgNi}_2$ ) as  $AB'A'C$ . We shall call these three structures 2-layer, 3-layer and 4-layer types respectively. The order in which the various types of layers can be stacked is restricted by the spatial requirements due to the large Mg atoms. Thus, an  $A$  layer can be followed only by  $B$  and  $B'$ . The possible ways of stacking the layers are shown in Table 2.

Table 2. Possible ways of layer stacking



Description of the Friauf-Laves phases and their stacking variants in terms of the six composite layers is analogous to that for cubic and hexagonal close packing and their stacking variants (e.g. lanthanum, samarium). In the latter case single layers are considered instead of composite layers. Moreover, the concept of positive and negative changes in close packing of spheres can be retained in the Friauf-Laves phases (Komura, Kishida & Inoue, 1967). In this sense the possible layer sequences of  $N$ -layer stacking can be constructed by the same method as in the close packing of spheres. (Patterson & Kasper, 1959). Since the present phase shows the 6-layer periodicity, possible sequences are limited only to the following two cases:

- (1)  $ABCA'C'B'$  ( $3\bar{3}$ )  
 (2)  $ABC'B'AB'$  ( $2\bar{2}1\bar{1}$ ).

The numbers of the Zhdanov symbols (in brackets) indicate the sequence of the number of positive and negative changes. Symmetry properties of stacked composite layers of the Friauf-Laves phases can be discussed as in the case of close packing of spheres. Thus, sequence No. 1,  $ABCA'C'B'$  is with the space group  $P6_3/mmc$ , while No. 2,  $ABC'B'AB'$  is  $P\bar{6}m2$ . The intensity distributions of the Friauf-Laves phases and

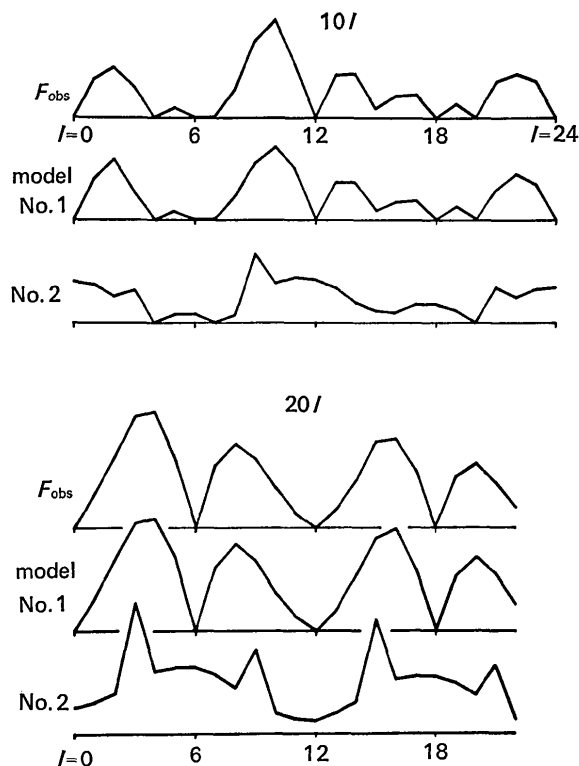


Fig. 3. Comparison of the observed and calculated structure factors of  $10l$  and  $20l$  reflexions for two stacking sequences.

their stacking variants have the following characteristics:

(1) For  $h-k=3n$  ( $n$  integral), only reflexions of  $l=NL$  ( $L$  integral) can be found, where  $N$  is the total number of stacked layers.

(2) For  $h-k=3n\pm 1$ , the intensity variation is found in two ways with respect to increasing index  $l$ . Observed reflexions of  $10l$  and  $20l$  are shown in Fig. 3 for comparison with calculation.

Referring to Fig. 2 the layer form factors of  $A$ ,  $A'$ ,  $B$ ,  $B'$ ,  $C$  and  $C'$  are given as

$$V_A = 2f_a \cos \frac{3}{8}\varphi + f_b [(-1)^h + (-1)^k + (-1)^{h-k}] + f_b \varepsilon \exp(i\varphi/2) \quad (1)$$

$$V_{A'} = 2f_a \cos \frac{3}{8}\varphi + f_b [(-1)^h + (-1)^k + (-1)^{h-k}] + f_b \varepsilon^* \exp(i\varphi/2) \quad (2)$$

$$V_B = V_A \varepsilon^* \quad V_{B'} = V_{A'} \varepsilon^* \quad V_C = V_A \varepsilon \quad V_{C'} = V_{A'} \varepsilon \quad (3)$$

where  $\varepsilon = \exp[2\pi i(h-k)/3]$ , phase shift  $\varphi = 2\pi l/6$ ,  $f_a$  is the atomic scattering factor for magnesium and  $f_b$  that for the smaller atom (Ni or Cu). When  $h-k=3n\pm 1$ , the structure factor of a given 6-layer sequence can be expressed as follows:

$$F_{\text{cal}}(hkl) = \sum_{m=0}^5 V_m \exp(im\varphi),$$

where  $V_m$  represents the layer form factor of the  $m$ th position. In Fig. 3 the observed and calculated structure factors of  $10l$  and  $20l$  reflexions for two kinds of

stacking sequences are compared. From Fig. 3 it can easily be seen that the correct sequence should be  $ABC'A'C'B'$ , for which 12 formula units of  $Mg(Ni_{0.45}Cu_{0.55})_2$  are contained in the hexagonal unit cell of the space group  $P6_3/mmc$ .

The positional parameters for the trial structure thus obtained are given in Table 3. The 36 atoms are placed in the 7 different positions, and nickel and copper atoms are assumed to be distributed at random in proportion to their composition.

Table 3. Atomic parameters of the trial structure

Ni, Cu(1) in 12( <i>k</i> )	$x, 2x, z$	$x_k = -\frac{1}{6}, z_k = \frac{1}{12}$
Ni, Cu(2) in 6( <i>h</i> )	$x, 2x, \frac{1}{4}$	$x_h = \frac{1}{2}$
Ni, Cu(3) in 4( <i>f</i> )	$\frac{1}{3}, \frac{2}{3}, z$	$z_{f1} = -\frac{1}{6}$
Ni, Cu(4) in 2( <i>a</i> )	0, 0, 0	
Mg(1) in 4( <i>f</i> )	$\frac{1}{3}, \frac{2}{3}, z$	$z_{f2} = \frac{7}{48}$
Mg(2) in 4( <i>f</i> )	$\frac{1}{3}, \frac{2}{3}, z$	$z_{f3} = \frac{1}{48}$
Mg(3) in 4( <i>e</i> )	0, 0, $z$	$z_e = \frac{3}{16}$

### Refinement of the structural parameters

The 7 positional parameters, the 7 isotropic temperature factors, and the scale factor were refined by full-matrix least-squares calculations using the program *ORFLS* of Busing, Martin & Levy (1962), modified by Sakurai to the UNICS system (1967). The atomic scattering factors listed in *International Tables for X-ray Crystallography* (1962) were employed, with the correction for anomalous dispersion. Nickel and copper atoms were assumed to be distributed at random among the small atom positions [12(*k*), 6(*h*), 4(*f*), 2(*a*)], and an average atomic scattering factor was used for these positions. Special subroutines were written in the program in order to take care of the atoms at special positions of different kinds. The 180 measured reflexions were used with unit weight, of which 82 were of zero intensity. After five cycles of the refinement, the *R* value (defined as  $\sum ||F_o| - |F_c|| / \sum |F_o|$ ) was 0.157 including zero reflexions and 0.114 omitting zero reflexions. Final atomic parameters and their estimated standard deviations are listed in Table 4. The observed and calculated structure amplitudes are given in Table 5.

### Results and discussion

A new stacking variant having a 6-layer sequence of  $ABC'A'C'B'$  has now been established in the pseudo-

binary system of  $MgNi_{2-55}$  mol%  $MgCu_2$ . Fig. 4 shows a schematic drawing of the structure, where the large white circles represent magnesium atoms and the small black circles show nickel or copper atoms. The positional parameters after the least squares refinement differ only slightly from the initial values, the amounts of shift being at most of the order of a thousandth of the unit cell.

Table 5. Observed and calculated structure factors

$h$	$k$	$l$	$F_o$	$F_c$	$F_o$	$F_c$	$F_o$	$F_c$	$F_o$	$F_c$	$F_o$	$F_c$	$F_o$	$F_c$	$F_o$	$F_c$
1	1	1	20	20	20	20	20	20	20	20	20	20	20	20	20	20
1	1	2	10	10	10	10	10	10	10	10	10	10	10	10	10	10
1	1	3	5	5	5	5	5	5	5	5	5	5	5	5	5	5
1	1	4	2	2	2	2	2	2	2	2	2	2	2	2	2	2
1	1	5	1	1	1	1	1	1	1	1	1	1	1	1	1	1
1	1	6	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	7	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	8	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	9	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	11	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	12	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	13	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	14	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	15	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	16	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	17	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	18	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	19	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	20	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	21	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	22	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	23	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	24	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	25	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	26	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	27	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	28	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	29	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	30	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	31	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	32	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	33	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	34	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	35	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1	1	36	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Magnesium to magnesium distances along the direction of [001] are considerably smaller than those along other directions. This means that the distance between two triangular magnesium nets adjacent to the kago-

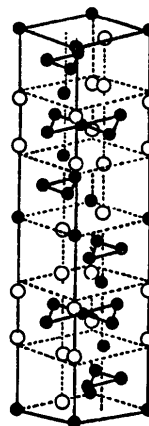


Fig. 4. The structure of the 6-layer stacking variant of Friauf-Laves phase, Mg-Cu-Ni. The layer sequence is  $ABC'A'C'B'$ .

Table 4. The final atomic parameters of  $MgNi_{2-55}$  mol %  $MgCu_2$  and their standard deviations

Atom	Position	$x$	$\sigma(x)$ ( $\times 10^4$ )	$y$	$\sigma(y)$ ( $\times 10^4$ )	$z$	$\sigma(z)$ ( $\times 10^4$ )	$B$
Ni, Cu(1)	12( <i>k</i> )	-0.1671	10	-0.3341	—	0.0835	3	0.53 Å <sup>2</sup>
Ni, Cu(2)	6( <i>h</i> )	0.4978	15	0.9956	—	$\frac{1}{4}$	—	0.47
Ni, Cu(3)	4( <i>f</i> )	$\frac{1}{3}$	—	$\frac{2}{3}$	—	-0.1672	6	1.16
Ni, Cu(4)	2( <i>a</i> )	0	—	0	—	0	—	1.21
Mg(1)	4( <i>f</i> )	$\frac{1}{3}$	—	$\frac{2}{3}$	—	0.1448	11	0.83
Mg(2)	4( <i>f</i> )	$\frac{1}{3}$	—	$\frac{2}{3}$	—	0.0233	13	1.82
Mg(3)	4( <i>e</i> )	0	—	0	—	0.1906	13	1.68

mé net are reduced compared with that of the trial layer structure.

Interatomic distances were computed using Sakurai's program of the UNICS system (1967) *RSDA-4*. They are listed in Table 6. Coordination numbers (CN) of the atoms are classified into two kinds. One is CN12 for copper or nickel atoms, which forms an icosahedron. The other is CN16 for Mg atoms, called the Friauf polyhedron after Samson (1958, 1961). These polyhedra are the same as the ones appearing in  $C_{14}$ ,  $C_{15}$  and  $C_{36}$ . The linkage of these polyhedra along the [001] direction through the cell origin is as follows:

CN12–CN16–CN16–CN12–CN16–CN16–CN12

Similar arrangements of fused polyhedra along the threefold axes are found in the  $\mu$ -phase and the  $R$ -phase (Komura, Sly & Shoemaker, 1960).

It is to be expected that the nickel and copper atoms are distributed regularly to form a superstructure. Although attempts have been made to prove this by neutron diffraction experiments on powder specimens of this compound, using the Kyoto University Reactor, superstructure reflexions could not be convincingly detected. The intensities of the possible superstructure

Table 6. *Interatomic distances*

Kind of atom	Ligancy	Distance (Å)	Kind of atom	Ligancy	Distance (Å)
Cu(1)	2Cu(1)	2.453 ± 8	Mg(1)	6Cu(1)	2.866 ± 15
	2Cu(1)	2.464 ± 8		3Cu(2)	2.891 ± 24
	1Cu(3)	2.459 ± 14		3Cu(3)	2.889 ± 5
	1Cu(4)	2.461 ± 7		1Mg(2)	2.920 ± 41
	2Mg(1)	2.866 ± 15		3Mg(3)	3.045 ± 15
	2Mg(2)	2.853 ± 17		16, Friauf polyhedron	
	1Mg(2)	2.933 ± 28			
	1Mg(3)	2.940 ± 28			
	12, icosahedron				
	Cu(2)	2Cu(2)		2.426 ± 12	Mg(2)
2Cu(2)		2.491 ± 12	3Cu(1)	2.933 ± 28	
2Cu(3)		2.456 ± 13	3Cu(4)	2.894 ± 6	
2Mg(1)		2.891 ± 24	1Mg(1)	2.920 ± 41	
4Mg(3)		2.844 ± 18	3Mg(2)	3.052 ± 16	
12, icosahedron		16, Friauf polyhedron			
Cu(3)	3Cu(1)	2.459 ± 14	Mg(3)	3Cu(1)	2.940 ± 28
	3Cu(2)	2.456 ± 13		6Cu(2)	2.844 ± 18
	3Mg(1)	2.889 ± 5		3Cu(3)	2.894 ± 7
	3Mg(3)	2.894 ± 7		3Mg(1)	3.045 ± 15
	12, icosahedron			1Mg(3)	2.858 ± 44
		16, Friauf polyhedron			
Cu(4)	6Cu(1)	2.461 ± 7			
	6Mg(2)	2.894 ± 6			
	12, icosahedron				

Table 7. *A list of stacking variants determined up to the present*

Layer type	Alloy system	Stacking order	Zhdanov symbol	ch-order
2-layer	MgZn <sub>2</sub>	AB'	1 $\bar{1}$	<i>h</i>
3-layer	MgCu <sub>2</sub>	ABC	(3)	<i>c</i>
4-layer	MgNi <sub>2</sub>	AB'A'C	2 $\bar{2}$	<i>ch</i>
6-layer	Mg–Ni–Cu	ABCA'C'B'	3 $\bar{3}$	<i>cch</i>
8-layer	Mg–Ni–Zn			
	Mg–Zn–Cu	AB'AB'A'CA'C	2 $\bar{1}$ 1 $\bar{2}$ 1 $\bar{1}$	<i>chhh</i>
9-layer	Mg–Zn–Ag			
	Mg–Cu–Al	AB'ABC'BCA'C	2 $\bar{1}$ 2 $\bar{1}$ 2 $\bar{1}$	<i>chh</i>
10-layer	Mg–Zn–Cu			
	Mg–Zn–Ag	ABC'BCA'C'BC'B'	2 $\bar{1}$ 2 $\bar{2}$ 1 $\bar{2}$	<i>chhch</i>
	Mg–Zn–Cu			

The existence of the 5-layer structure reported in Mg–Cu–Al system (Komura, 1962) is in doubt for it may be a 10-layer structure as found in other alloy systems. Reinvestigations are now in process, and, therefore, the 5-layer structure is omitted from this table.

reflexions with the same space group are calculated to be very weak for the powder sample. Because a single crystal appropriate for neutron diffraction work was not available, therefore, the existence of the superstructure could not be confirmed.

As stated before, this phase was found in the range of the mixture of  $C_{15}$  and  $C_{36}$  according to Lieser & Witte. The structure was concluded to be a new stacking variant. The stable range of this phase is in the vicinity of 50 to 55 mol%  $MgCu_2$ . From this fact the phase diagram proposed by Lieser & Witte has to be corrected as shown in Fig. 1, where the hatched region is the stabilization range of the new six-layer stacking variant.

In the course of our investigation of the Mg-based ternary Friauf-Laves phases, a very similar powder diffraction pattern was also found in a sample of  $MgNi_2$ -27.5 mol%  $MgZn_2$  corresponding to the mixed region of  $C_{15}$  and  $C_{36}$  (Lieser & Witte, 1952). The structure was concluded to be isomorphous with the structure analyzed in this paper. The new stacking variant of the 6-layer sequence appears at approximately the same electron concentration in both systems, though the mol% of  $MgCu_2$  and  $MgZn_2$  is different. The relation between electron concentration and crystal structure in the Mg-based ternary systems will be discussed in detail in a further publication. The stacking variants found in several pseudo-binary systems are summarized in Table 7, in which the layer sequences are represented by *ch*-order as well as Zhdanov symbol, and the first three correspond to the Friauf-Laves structures.

The six-layer stacking variant is also found in the Au-Cd system (Hirabayashi, Hiraga, Yamaguchi & Ino, 1969), but the layer sequence in this system corresponds to the sequence No. 2 ( $ABC'B'AB'$ ) described in the present paper.

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## Struktur eines Cyclopentaphosphates

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The structure of the cyclopentaphosphate  $Na_4(NH_4)P_5O_{15} \cdot 4H_2O$  was determined by the symbolic addition procedure. The crystals are triclinic,  $P\bar{1}$ , with  $a = 8.73$ ,  $b = 15.66$ ,  $c = 6.81$  Å,  $\alpha = 93.9^\circ$ ,  $\beta = 106.1^\circ$ ,  $\gamma = 95.1^\circ$ . The phosphorus atoms of the ring are arranged in a chair conformation.

### Einleitung

Von Thilo & Schülke (1965) wurden in Grahamschem Salz Cyclophosphate mit Ringgrößen von  $(P_3O_9)^{3-}$  bis  $(P_8O_{24})^{8-}$  nachgewiesen und zum Teil auch isoliert.

Das höchste Glied mit ungerader Zahl von Phosphoratomen im Ring, welches in reiner Form erhalten wurde, ist das Cyclopentaphosphat. Von dessen Natriumsalz, welches von U. Schülke dargestellt wurde, waren bereits vor längerer Zeit von W. Hilmer Rönt-