References

CATANI, A. & ZANAZZI, P. F. (1965). *Ric. Sci.* **35** (II-*A*), 524.
COX, E. G. & JEFFREY, G. A. (1951). *Proc. Roy. Soc.* A**207**, 110.
FIGGIS, B. N. (1966). *Introduction to Ligand Fields*. New York: Interscience.
FRANZINI, M. & SCHIAFFINO, L. (1962). *Mem. Soc. tosc. Sci. nat.* **69**, 342.
HOSKINS, B. I. & KELLY, B. P. (1970). *Chem. Commun.* p. 45.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
MAZZI, F., TAZZOLI, V. & UNGARETTI, L. (1969). *Mem. Accad. Lincei*, **47**, 69.
MERLINO, S. (1969). *Acta Cryst.* B**25**, 2270.
MERLINO, S. (1972). In the press.
PALM, J. H. (1964). *Acta Cryst.* **17**, 1326.
PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
PEARSON, W. B. (1965). *Z. Kristallogr.* **121**, 449.
SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.
STEWART, J. M. (1964). *Crystal Structure Calculations System, X-Ray* 63. Tech. Rep. TR-64-6, Computer Science Center, Univ. of Maryland and Research Computer Laboratory, Univ. of Washington.
Tables of Interatomic Distances and Configuration in Molecules and Ions (1958). Special Publication No. 11. London: The Chemical Society.
Tables of Interatomic Distances and Configuration in Molecules and Ions (1965). Special Publication No. 18. London: The Chemical Society.
WATANABE, Y. & YAMAHATA, K. (1970). *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **64**, 71.

Acta Cryst. (1972). B**28**, 976

The Relation between Electron Concentration and Stacking Variants in the Alloy Systems Mg-Cu-Ni, Mg-Cu-Zn and Mg-Ni-Zn

BY Y. KOMURA, M. MITARAI, A. NAKAUE AND S. TSUJIMOTO

Faculty of Science, Hiroshima University, Higashi-Senda-Machi, Hiroshima, Japan

(*Received* 14 *July* 1971)

In the pseudo-binary systems $MgNi_2$–$MgZn_2$ four new stacking variants were found in the mixed region of C_{36} and C_{15} and of C_{15} and C_{14} in the phase diagram given by Lieser, K. H. & Witte, H. (*Z. Metallk.* (1952) **43**, 396). These four stacking variants are isomorphous with the ones found in the systems $MgCu_2$–$MgNi_2$ and $MgCu_2$–$MgZn_2$. Homogeneity ranges of the various stacking variants among above three systems were shown as a function of electron concentration. A remarkable correspondence was found in the relation between electron concentration and crystal structure. The following structures are given in order of increasing e/a: 4-layer, 6-layer, 3-layer, 4-layer, 10-layer, 9-layer, 8-layer and 2-layer type structure. The relation between the electron concentration and the stabilization of stacking variants is evident in these Mg-base ternary alloy systems.

Among several factors governing the crystal structure of alloy phases, the electron concentration is important for the stabilization of long period anti-phase domains (Sato & Toth, 1961, 1962) and of long period stacking order in several alloy systems (Sato, Toth, Shirane & Cox, 1966; Sato, Toth & Honjo, 1967; Sato & Toth, 1968; Pearson, 1970). The origin of the stabilization of the structure has been understood as being due to the creation of Brillouin zone boundaries at the Fermi surface. Stacking variants of the Friauf–Laves phases seem to be another example of structures resulting from this phenomenon.

Laves & Witte (1936) and Lieser & Witte (1952) reported a relationship between electron concentration and the crystal structure of Mg-base ternary Friauf–Laves phases. They discussed structural changes of Friauf–Laves phases as a function of e/a (the electron-atom ratio). For example, when Cu atoms in $MgCu_2$ are replaced by other metal of different valency, the cubic $C_{15}(MgCu_2)$ type structure is changed to the hexagonal $C_{14}(MgZu_2)$ type or $C_{36}(MgNi_2)$ type structures depending upon the electron concentration. Although they discussed only three fundamental structures of C_{14}, C_{15} and C_{36}, Komura, Mitarai, Nakatani, Iba & Shimizu (1970) reported similar relationships including three new stacking variants in addition to C_{14}, C_{15} and C_{36} for the systems of Mg–Zn–Cu and Mg–Zn–Ag. These new structures are called 8-, 9- and 10-layer types on the basis of the layer stacking. Komura, Nakaue & Mitarai (1972) found another new stacking variant of the 6-layer type in the system Mg–Cu–Ni. We undertook a reinvestigation of the work of Lieser & Witte (1952) for the three ternary systems Mg–Cu–Zn, Mg–Ni–Zn and Mg–Cu–Ni in order to see the dependence of the structural change on the electron concentration in more detail, and also to study the possibility of finding new stacking variants in the system of Mg–Ni–Zn as in the case of Mg–Cu–Zn and Mg–Cu–Ni.

The structures of Friauf–Laves phases and their stacking variants can be described in terms of the stacking sequence of six kinds of compound layers (Komura, 1962). These six layers are called *A*, *A'*, *B*, *B'*, *C* and *C'*, each of which is composed of a Kagomé net and three triangular nets. Layer stacking of these compound layers conforms to the spatial requirements of large Mg atoms, each layer can be followed only by the other two layers. For example, an *A* layer is followed only by *B* and *B'*. The stacking variants which were found up to the present in Mg-base pseudo-binary systems are listed as follows:

Layer type	Stacking order
2-layer (C_{14}–$MgZn_2$)	*AB'*
3-layer (C_{15}–$MgCu_2$)	*ABC*
4-layer (C_{36}–$MgNi_2$)	*AB'A'C*
6-layer	*ABCA'C'B'*
8-layer	*AB'AB'A'CA'C*
9-layer	*AB'ABC'BCA'C*
10-layer	*ABC'BCA'C'BC'B'*

Alloy system $MgNi_2$–x % $MgZn_2$

Fifteen specimens covering the whole range of the system were prepared by melting pure metals of Mg, Zn, carbonyl Ni powder and Mg–50% Ni mother-alloy together in an argon-filled induction furnace or in the presence of flux ($MgCl_2$,KCl,NaCl mixture) in order to prevent oxidation. The compositions were checked for three specimens by chemical analysis. The results are given in Table 1.

After annealing the specimens for 5 days under argon atmosphere in a fused silica tube at about 400 °C, X-ray powder diffraction patterns were examined using these specimens. The results of Lieser & Witte (1952) were confirmed in the regions of single phase of C_{36}, C_{15} and C_{14}; C_{36} for $x=0\sim20\%$, C_{15} for $x=30\sim80\%$ and C_{14} for $x=97\sim100\%$ $MgZn_2$. Besides these phases, however, four new phases were found in relatively narrow regions in the mixture range of two phases according to Lieser & Witte. The structures of these new phases were analysed by comparing the observed and calculated intensities of X-ray powder diffraction patterns. These were found to be a 6-layer structure (*ABCA'C'B'*) in the vicinity of $x=27{\cdot}5\%$, a 4-layer structure (*AB'A'C*) for $x=85\sim92\%$, a 10-layer structure (*ABC'BCA'C'BC'B'*) for $x=95\%$ and a 9-layer structure (*AB'ABC'BCA'C*) for $x=95{\cdot}5\%$. These four phases are isomorphous with the ones found in Mg–Cu–Ni and Mg–Cu–Zn (Komura, Kishida & Inoue, 1967; Komura *et al.*, 1970; Komura *et al.*, 1972). The phase diagram proposed by Lieser & Witte for this system has to be corrected for the above four new phases.

Structural changes in the three alloy systems Mg-Cu-Ni, Mg-Cu-Zn and Mg-Ni-Zn

When Ni is replaced by Zn in the system $MgNi_2$–x% $MgZn_2$, the electron concentration is changed from 0·67 *e*/*a* ($MgNi_2$) to 2·00 *e*/*a* ($MgZn_2$) provided that the valency of the Ni atom is to be zero. The variation of electron concentration in this system is wide and covers the change of *e*/*a* of the systems $MgNi_2$–$MgCu_2$ and $MgCu_2$–$MgZn_2$. Structural changes in the system of $MgNi_2$–$MgZn_2$ as a function of *e*/*a* is shown in Fig. 1 compared with the variation of structures in the systems $MgNi_2$–$MgCu_2$ and $MgCu_2$–$MgZn_2$. From an inspection of this diagram it was found that the all stacking variants including newly discovered

Table 1. *Composition of the alloy specimens* (*wt.* %)

	Mg		Ni		Zn	
	Analysed	Prepared	Analysed	Prepared	Analysed	Prepared
$MgNi_2$–27·5% $MgZn_2$	16·3%	16·7%	58·4%	58·6%	25·3%	24·7%
$MgNi_2$–95·0% $MgZn_2$	15·5	15·7	3·7	3·8	80·8	80·5
$MgNi_2$–95·5% $MgZn_2$	16·0	15·8	3·4	3·4	80·6	80·8

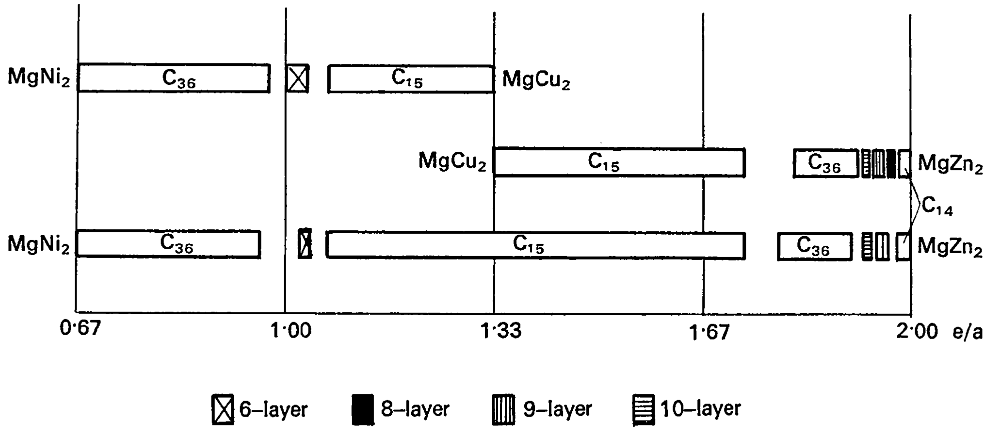

Fig. 1. Structural changes in the Mg–Cu–Ni, Mg–Cu–Zn and Mg–Ni–Zn alloys as a function of the electron; atom ratio.

Table 2. *Lattice constants of the 4-layer type structures*

Specimen	*a*	*c*	*c*/*a*
$MgNi_2$	4·834 ± 0·002 Å	15·798 ± 0·002 Å	3·268
$MgNi_2$–40 % $MgCu_2$	4·903 ± 0·001	15·962 ± 0·002	3·255
$MgNi_2$–90 % $MgZn_2$	5·163 ± 0·001	16·955 ± 0·002	3·284

Table 3. *Stacking variants of Mg-base ternary Friauf-Laves phases*

e/*a*	Stacking order	Zhdanov symbol	*ch* order	Fraction of *h* sequence
0·67 to 0·97	*AB′A′C*	$2\bar{2}$	*chch*	0·50
1·00	*ABCA′C′B′*	$3\bar{3}$	*cchcch*	0·33
1·07 to 1·73	*ABC*	3	*ccc*	0
1·80 to 1·89	*AB′A′C*	$2\bar{2}$	*chch*	0·50
1·93	*ABC′BCA′C′BC′B′*	$2\bar{1}2\bar{2}1\bar{2}$	*hhchchhchc*	0·60
1·95	*AB′ABC′BCA′C*	$2\bar{1}2\bar{1}2\bar{1}$	*chhchhchh*	0·67
1·98	*AB′AB′A′CA′C*	$1\bar{2}1\bar{1}2\bar{1}$	*hhhchhhc*	0·75
2·00	*AB′*	$1\bar{1}$	*hh*	1·00

ones appear in nearly the same *e*/*a* values for all systems. Although an 8-layer structure could not be found in Mg–Ni–Zn, it is probable that the relevant stabilization range exists but is extremely narrow, and therefore difficult to detect. The effect of the electron concentration on the stabilization of long period stacking variants is evident in these Mg-base ternary alloys based on the diagram in Fig. 1.

Accurate lattice constants were measured for three specimens having 4-layer type structure using single-crystal Weissenberg photographs on which powder patterns of Si were recorded as a standard. The results are listed in Table 2.

Table 3 summarizes the relation between various stacking variants and *e*/*a* together with the representation by Zhdanov symbol, *ch*-order and the fraction of the *h* sequence. The fraction of the *h* sequence decreases with increasing *e*/*a* in the range 0·67 ~ 1·73 *e*/*a*, but increases with increasing electron concentration. The interpretation of this result is in progress on the basis of Sato & Toth's theory.

This work has partly been supported by a Scientific Research Grant of the Ministry of Education, to which the authors' thanks are due.

References

Komura, Y. (1962). *Acta Cryst.* **15**, 770.

Komura, Y., Kishida, E. & Inoue, M. (1967). *J. Phys. Soc. Japan* **23**, 398.

Komura, Y., Mitarai, M., Nakatani, I., Iba, H. & Shimizu, T. (1970). *Acta Cryst.* B**26**, 666.

Komura, Y., Nakaue, A. & Mitarai, M. (1972). *Acta Cryst.* B**28**, 727.

Laves, F. & Witte, H. (1936). *Metallwirtschaft*, **15**, 840.

Lieser, K. H. & Witte, H. (1952). *Z. Metallk.* **43**, 396.

Pearson, W. B. (1970). *Acta Cryst.* B**26**, 1044.

Sato, H. & Toth, R. S. (1961). *Phys. Rev.* **124**, 1833.

Sato, H. & Toth, R. S. (1962). *Phys. Rev.* **127**, 469.

Sato, H., Toth, R. S., Shirane, G. & Cox, D. E. (1966). *J. Phys. Chem. Solids* **27**, 413.

Sato, H., Toth, R. S. & Honjo, G. (1967). *J. Phys. Chem. Solids* **28**, 137.

Sato, H. & Toth, R. S. (1968). *Acta Met.* **16**, 413.