Table 6. *Intermolecular distances less than* 4 Å

The following Roman numbers give the symmetry relationship of the atoms concerned

	x	y	z			x	y	z
I	x	y	z	VI		$\frac{1}{2}+x$	$\frac{1}{2}+y$	z
II	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$-z$	VII		$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
III	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	VIII		$-x$	$1-y$	$-z$
IV	$-x$	$-y$	$-z$	IX		x	$1+y$	z
V	$1-x$	y	$\frac{1}{2}-z$	X		$\frac{1}{2}-x$	$-\frac{1}{2}-y$	$-x$

i		j		$d(ij)$	i		j		$d(ij)$
C(1)	I	C(2)	II	3·796 Å	C(7)	I	O(1)	IV	3·407 Å
C(1)	I	C(8)	II	3·607	C(7)	I	O(2)	IV	3·477
C(1)	I	C(9)	III	3·721	C(8)	I	C(8)	X	3·649
C(2)	I	C(2)	II	3·684	C(8)	I	O(1)	II	3·816
C(2)	I	C(7)	II	3·989	C(9)	I	C(9)	V	3·910
C(2)	I	C(8)	II	3·811	C(9)	I	O(2)	VI	3·998
C(2)	I	O(1)	II	3·881	C(9)	I	O(2)	VII	3·963
C(3)	I	C(5)	III	3·898	C(10)	I	O(1)	VIII	3·740
C(3)	I	C(7)	II	3·742	C(10)	I	O(2)	IX	3·523
C(3)	I	O(1)	II	3·388	O(1)	I	O(1)	IV	3·372
C(6)	I	C(8)	II	3·731	O(1)	I	O(2)	IV	2·648*
C(6)	I	C(9)	III	3·776	O(2)	I	O(2)	IV	3·538
C(7)	I	C(7)	IV	3·869					

* Hydrogen bond.

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Structural Changes in the Alloy Systems of Mg–Zn–Cu and Mg–Zn–Ag Related to the Friauf–Laves Phases

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In the pseudo-binary alloy systems of $MgZn_2$–$MgCu_2$ and $MgZn_2$–$MgAg_2$ three new stacking variants were found in the homogeneity ranges of the C_{14} and C_{36} structures. These three structures can be expressed, in terms of the stacking sequence of six compound layers, as 8-layer $(AB'AB'A'CA'C)$, 9-layer $(AB'ABC'BCA'C)$ and 10-layer $(ABC'BCA'C'BC'B')$ type. Representation of the Friauf–Laves phases and of relevant layer structures is discussed in connexion with that of the closest packing of spheres.

Among several factors governing the crystal structures of alloy phases or intermetallic compounds, the electron concentration is 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* and found that,

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* The term 'Friauf–Laves phases' is used in this paper for the C_{14}, C_{15} and C_{36} type structures, since there has been confusion in specifying these types of phase. The structures of $MgCu_2$ and $MgZn_2$ were originally determined by Friauf (1927a,b) and that of $MgNi_2$ by Laves & Witte (1935). New stacking variants reported in this paper are classified in terms of structures related to Friauf–Laves phases. (We are grateful for Dr S. Samson's suggestion on this point.)
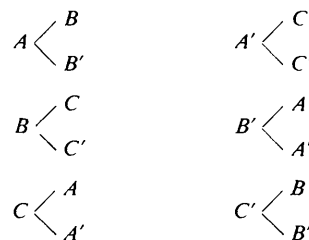
when, for instance, Cu in $MgCu_2$ is replaced by a metal of higher valency, such as Zn, Al or Si, the cubic C_{15} ($MgCu_2$) structure is followed by the C_{36} ($MgNi_2$) and C_{14} ($MgZn_2$) structures as the electron-atom ratio (e/a) is increased. This work indicated a close relationship between electron concentration and crystal structure, because the phase boundaries for the above three types of structure appeared at almost the same electron concentration for various combinations of metals.

We re-investigated the pseudo-binary systems of $MgZn_2$–$MgCu_2$, $MgZn_2$–$MgAg_2$, $MgCu_2$–$MgAl_2$, $MgCu_2$–$MgSi_2$ and $MgCu_2$–$MgNi_2$, and confirmed that the crystal structures of the systems Mg–Zn–Cu and Mg–Zn–Ag were strongly governed by the electron

concentration. In addition, three new stacking variants of Friauf–Laves phases were found between the homogeneity ranges of $MgZn_2$ and $MgNi_2$ type structures. These three new stacking variants are called 8-, 9- and 10-layer type, on the basis of factors discussed below. The structure of the 9-layer type is the same as that found in Mg–Cu–Al (Komura, 1962) and the 10-layer structure is the same as that reported by Komura, Kishida & Inoue (1967) for the system of Mg–Zn–Ag. The structure of the 8-layer type will be reported in the near future.

The structures of Friauf–Laves phases and their stacking variants can be described in terms of the stacking sequence of the six compound layers A, A', B, B', C and C', each of which is composed of a Kagomé net and three triangular nets as shown in Fig. 1 (Komura, 1962). The layer stacking conforms to the spatial requirements of the large Mg atoms: for example, an A layer can be followed only by B and B'. The possible ways of stacking the layers are shown in Table 1. Thus, e.g. C_{14}–$MgZn_2$ may be described as AB', C_{15}–$MgCu_2$

as ABC and C_{36}–$MgNi_2$ as $AB'A'C$, and these structures may be called 2-layer, 3-layer and 4-layer type respectively.

Table 1. *Possible ways of layer stacking*

$$A\Big\langle {}^B_{B'} \qquad A'\Big\langle {}^C_{C'}$$

$$B\Big\langle {}^C_{C'} \qquad B'\Big\langle {}^A_{A'}$$

$$C\Big\langle {}^A_{A'} \qquad C'\Big\langle {}^B_{B'}$$

When Zn is replaced by Cu or Ag in $MgZn_2$ as in the work described here, the 2-layer structure persists up to about $1\cdot98$ e/a, and is followed by the new stacking variants of the 8-layer, 9-layer and 10-layer structures. The known 4-layer and 3-layer structures occur thereafter from about $1\cdot92$ e/a. Fig. 2 summarizes the structural changes in the systems $MgZn_2$–$MgCu_2$ and $MgZn_2$–$MgAg_2$. Comparison between the two systems shows a striking correspondence with regard to the relation between electron concentration and crystal structure. Space groups and layer stacking sequences of the three new stacking variants are given in Table 2 together with the lattice constants.

Description of the Friauf–Laves phases and their stacking variants in terms of the layer stacking sequence of six compound layers is closely related to the closest packing of spheres. The only difference is in the kinds of layer; each of the compound layers A, A', $\cdots$ is composed of four nets, in contrast with the single layer, A, B or C, in a close packed structure. However, the concepts of positive and negative changes in the closest packing of spheres can be extended to the Friauf–Laves phases. For instance, corresponding to the sequences $A \to B$ and $A \to C$ in the case of spheres, $A \to B$ and $A \to B'$ may be called the positive and negative change respectively (Komura, Kishida & Inoue, 1967). Thus, for instance, the representation of stacking in terms of ch-order, developed by Jagodzinski (1949), is also applicable to the stacking of compound layers; in this case c and h stand for positive and negative change respectively. Pearson & Shoemaker (1969) proposed another way of describing these structures in terms of zigzag lines (L and R) along the direction of stacking of the layers. However, description based on the stacking sequence of compound layers has the advantage that calculation of the structure factors can be carried out by simply writing down the layer form factors with appropriate phase shifts corresponding to the stacking order of the layers.

The close relationship between Brillouin-zone boundaries of the Friauf–Laves phases and the Fermi surface, and electron concentration, will be discussed in the near future.
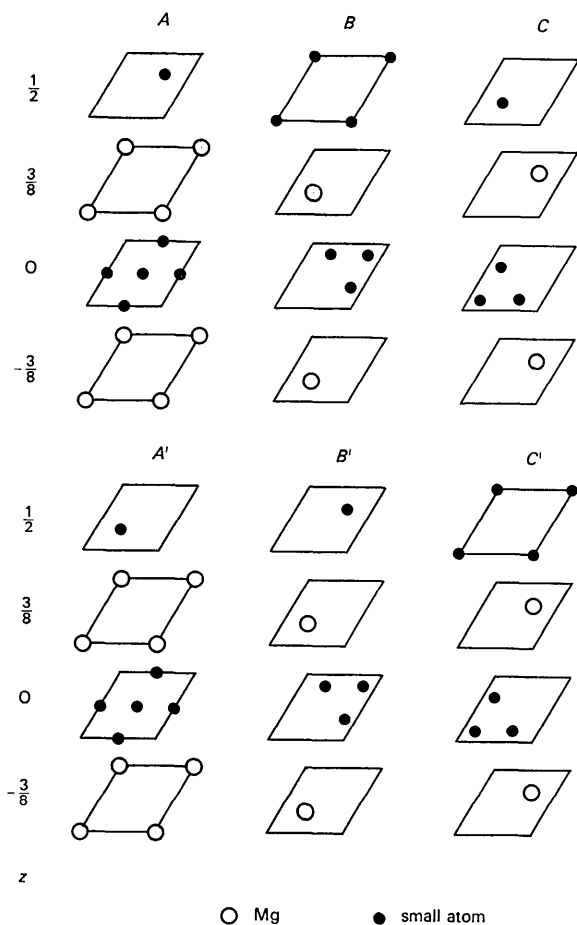

○ Mg   ● small atom

Fig. 1. Six kinds of compound layer of the Friauf–Laves phases. The parameter z is taken as a fraction of the distance between two Kagomé nets.

Table 2. *Crystal data for the three new stacking variants*

			Lattice constants (Å)†	
Layer type	Space group	Stacking order	Mg–Zn–Cu	Mg–Zn–Ag
8-layer	$P6_3/mmc$	$AB'AB'A'CA'C$	$a= 5{\cdot}21$	$a= 5{\cdot}21$
			$c=34{\cdot}2$	$c=34{\cdot}4$
9-layer	$R\bar{3}m$	$AB'ABC'BCA'C$	$a= 5{\cdot}19$	$a= 5{\cdot}21$
			$c=38{\cdot}4$	$c=38{\cdot}7$
10-layer	$P6_3/mmc$	$ABC'BCA'C'BC'B'$	$a= 5{\cdot}17$	$a= 5{\cdot}22$
			$c=42{\cdot}5$	$c=43{\cdot}0$

† All the lattice constants are given for a hexagonal unit cell.
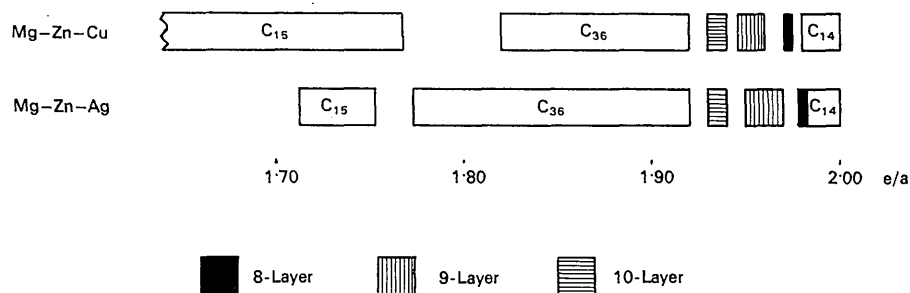
Fig. 2. Structural changes in the Mg–Zn–Cu and Mg–Zn–Ag alloys as a function of the electron-atom ratio.

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Remeasurements of the Structure of
Potassium-2,2,5,5-tetramethyl-3-carboxypyrroline-1-oxyl

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The structure of the nitroxide free radical, $C_9H_{13}NO_3K.\frac{1}{2}H_2O$ has been redetermined using data obtained for the full copper sphere with an automatic single-crystal diffractometer and Mo $K\alpha$ X-radiation. There are two independent molecules of the radical per asymmetric unit and after refinement to $R=0{\cdot}07$ these were found to be identical and planar within experimental error. The irregularities observed in a previous investigation, particularly an abnormally short C–C bond which occurred in both crystallographically independent molecules in the asymmetric unit, did not recur and the expected molecular symmetry was observed.

Introduction

A crystal of the potassium salt of 2,2,5,5-tetramethyl-3-carboxypyrroline-1-oxyl was used previously (Kruger & Boeyens, 1968) to determine the geometry of a sterically protected nitroxide radical incorporated in a five-membered ring. This system is important as a spin label (Hamilton & McConnell, 1968) and accurate structure parameters are desirable.

Because of insufficient data certain irregularities were observed, particularly for bonds lying parallel to [010]. The fact that one particular bond was similarly