transition metal atoms in the plane and six above and below it in planar kagomé nets (*i.e.* nets with only 3636 tessellations). In the present structure there are in the mirror planes rhombs formed by Nd atoms which are surrounded by B and Fe atoms. The sigma-phase nets (which contain 3636, 6^3, and 3^26^2 tessellations) above and below the mirror plane are severely puckered in such a way that Fe(6) (which is above and below a B—B connected line) is 1·1 Å closer to that plane than the pair of Fe(5) atoms (which lies above and below the Nd rhomb).

The structure of $Nd_2Fe_{14}B$ also resembles that of Mn_5SiC (Spinat, Fruchart, Kabbani & Herpin, 1970), which consists of two layers and one subsidiary layer of Laves-type structure ($MgZn_2$, C14), sandwiched between mirror planes which are less densely populated by Mn and C atoms. In this case the puckered sigma-phase nets in $Nd_2Fe_{14}B$ consisting of *hexagons* and triangles are replaced by less puckered nets of *pentagons* and triangles which occur in $MgZn_2$ perpendicular to [110] (Shoemaker & Shoemaker, 1967). In both cases the 'interstitial' atoms (B in $Nd_2Fe_{14}B$ and C in Mn_5SiC) are in trigonal prisms connecting pairs of double layers together.

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A New Ordered Structure of the *C*15-Type Laves Phase, $Mg_{28.4}Cu_{57.9}Si_{13.7}$

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Abstract. $M_r/100 = 47\cdot54$, cubic, space group $P4_132$ (or $P4_332$), $a = 6\cdot9598\,(4)$ Å, $V = 337\cdot12$ Å^3, $D_m = 5\cdot66\,(2)$, $D_x = 5\cdot62$ Mg m^{-3}, 24 atoms per unit cell, $\lambda(\text{Mo } K\alpha) = 0\cdot7107$ Å, $\mu(\text{Mo } K\alpha) = 22\cdot8$ mm^{-1}, $F(000) = 530\cdot7$, $R(F) = 0\cdot046$ for 82 independent reflections, room temperature. A new ordered structure of the Laves phase was found at the off-stoichiometric composition Mg_2Cu_3Si. The structure is characterized by ordered fourfold screw arrangements of Cu and Si atoms located on four tetrahedra in the unit cell leaving Mg atoms on 8(*c*) sites. The order parameter $S = \alpha_1 - \alpha_2$ is estimated from the refinement of the structure to be 0·74 in this specimen; α_1 and α_2 are the occupancy factors of Cu on sites 12(*d*) and 4(*a*) of $P4_132$, respectively.

Introduction. Laves phases are classified into the three fundamental structures *C*14, *C*15 and *C*36 which are typified by $MgZn_2$, $MgCu_2$ and $MgNi_2$, respectively. These structures were analyzed by Friauf (1927*a*,*b*) and Laves & Witte (1935). The pseudo-binary system $MgCu_2$–$MgSi_2$ has been studied thoroughly by Witte (1939). In this system the terminal solid solution of the cubic *C*15 type ($MgCu_2$ structure) extends from $MgCu_2$ to 20% $MgSi_2$; the hexagonal *C*14 type ($MgZn_2$ structure) then follows in the range 25–35% $MgSi_2$. The structure of the latter phase whose ideal composition is Mg_2Cu_3Si has shown an ordered arrangement of Cu and Si in the 6(*h*) and 2(*a*) sites, respectively, in $P6_3/mmc$. Moreover, a disordered *C*36-type structure was found as a high-temperature phase of the Mg_2Cu_3Si compounds. Witte (1939) also found a compound ($Mg_6Cu_{16}Si_7$) having the $D8_a$-type structure away from the pseudo-binary section of MgX_2. Ellner & Predel (1979) have carried out X-ray and neutron

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Table 1. *Parameters obtained for ordered* $Mg_{28.4}Cu_{57.9}Si_{13.7}$

	Site	*x*	*y*	*z*	*B*(Å^2)	α_i
$Mg_{0.85}Cu_{0.15}$	8(*c*)	0·00320 (64)	*x*	*x*	0·98 (10)	
α_1Cu.(1−α_1)Si	12(*d*)	$\frac{1}{8}$	0·13092 (22)	$x+\frac{1}{4}$	0·63 (6)	0·979 (10)
α_2Cu.(1−α_2)Si	4(*a*)	$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{8}$	0·54 (18)	0·237 (30)

diffraction examinations on polycrystalline Laves phases of *C*15 type in the systems $MgCu_2$–$MgZn_2$, $MgCu_2$–$MgNi_2$ and $MgNi_2$–$MgZn_2$. They found no indication of structural change or ordering within the existence range of the solid solutions.

In the present study, a new phase with an ordered structure of *C*15 type was found in the ternary system Mg–Cu–Si: $Mg_{28.4}Cu_{57.9}Si_{13.7}$, which is off-stoichiometric from a Laves-phase composition Mg_2Cu_3Si. The order parameters of the specimen were estimated by full-matrix least-squares refinements of the structure including occupancy factors for each site.

Experimental. From preliminary experiments the region where the *C*15-type ordered phase is stable was found at the off-stoichiometric composition MgX_2. The composition of the specimen examined was $Mg_{28.4}$-$Cu_{57.9}Si_{13.7}$. The alloy ingot was prepared by melting pure Mg and Cu metals and Cu–Si mother alloy in an electrical-resistance furnace at 1270 K in the presence of flux (NaCl, KCl and $CaCl_2$ mixture) in order to prevent oxidation. The alloy ingot thus obtained was annealed for 10 d at 770 K ($T_c \simeq 870$ K from the preliminary experiment) in an argon-filled sealed silica tube. The composition of the alloy specimen was checked by atomic absorption measurement. A tiny single-crystal fragment of irregular shape (approximate sphere, radius 0·05 mm) was selected from the crushed ingot. Density measured pycnometrically. Laue and Weissenberg photographs showed Laue group *m*3*m*, systematic absences $l \neq 4n$ for 00*l*, indicating space group $P4_132$ or $P4_332$. Cell constants estimated from 25 interplanar spacings measured on the X-ray diffractometer with a least-squares fit. Reflection data with $|F| > 3\sigma(F)$ collected in the range $2\theta < 50{\cdot}0°$. Rigaku AFC-5 automated diffractometer, graphite-monochromated Mo *Kα* radiation. θ–2θ-scan mode, scan speed 2° min^{-1}, scan range $(1{\cdot}2 + 0{\cdot}5\tan\theta)°$. Backgrounds measured by stationary counting at the scan extremes for 2 s each. Reflections 800, 080, 008, $\bar{8}00$, $0\bar{8}0$, $00\bar{8}$ chosen as internal standards and measured every 100 reflections. Monitor-counting method adopted in order to decrease the influence of the primary-beam fluctuation. Lorentz–polarization corrections, but no absorption correction ($\mu r \simeq 1{\cdot}1$). After averaging of symmetry-related reflections 82 independent reflections used for structure analysis. Atomic scattering factors for Mg, Cu and Si atoms and f' and f'' values from *International Tables for X-ray Crystallography* (1974). Structural parameters refined with the full-matrix least-squares program *RSFLS*-4 (*UNICS*, 1967) and unit weight for all $|F|$'s. With Lagrange's unknown-multiplier method (Okamura, Iwasaki & Ogawa, 1968), the *RSFLS* program was modified to be able to refine the order parameters α_1 and α_2, which are occupancy factors for Cu atoms at sites 12(*d*) and 4(*a*), respectively. A scale factor, positional parameters and isotropic temperature factors for all atoms were then refined; $R(F) = 0{\cdot}046$, $S = 0{\cdot}6655$, $(\Delta/\sigma)_{\max} = 0{\cdot}12$, final $\Delta\rho$ excursions $\leq |9{\cdot}5|$ e Å^{-3}.

Discussion. The final parameters are listed in Table 1.* Here it is assumed that site 8(*c*) is occupied by all the Mg atoms and by the excess (with respect to the composition MgX_2) Cu atoms. The *C*15-type $MgCu_2$ crystal belongs to space group *Fd*3*m*, whereas the newly found ordered modification of *C*15 type crystallizes in space group $P4_132$ (or $P4_332$). No effort has been made to distinguish between 4_1 and 4_3 in the present study. The Cu-site 16(*d*) positions in *Fd*3*m* split into two independent sites 4(*a*) and 12(*d*) in $P4_132$ for Cu and Si atoms. The ordered structure is characterized by the ordered fourfold screw arrangements of Cu and Si atoms located on four tetrahedra in the unit cell, leaving Mg atoms on site 8(*c*). The 8(*c*) site is assumed to be occupied by all the Mg atoms and by the excess Cu atoms randomly. A stereoscopic view of the ordered structure is shown in Fig. 1 (*ORTEP*; Johnson, 1976).

The structure is closely related to that of the compound Al_2Mo_3C whose structure was analyzed by Jeitschko, Nowotny & Benesovsky (1962). The structure of this compound belongs to $P4_132$, and Al, Mo and C atoms are located respectively on sites 8(*c*), 12(*d*) and 4(*a*), just as in the present ordered phase. However, the structural parameters of sites 8(*c*) and 12(*d*) of Al_2Mo_3C differ considerably from the ordered Laves phase. In addition, if we allot Mg, Cu and Si

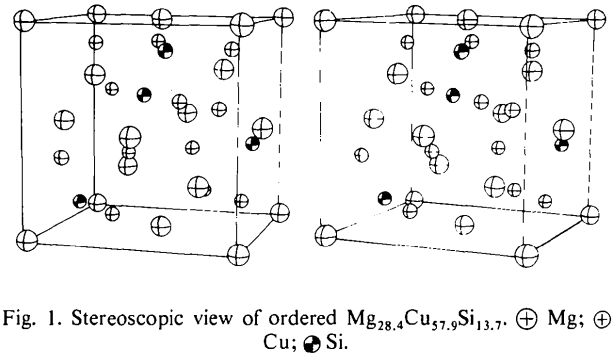

Fig. 1. Stereoscopic view of ordered $Mg_{28.4}Cu_{57.9}Si_{13.7}$. ⊕ Mg; ⊕ Cu; ● Si.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39573 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

atoms to the positions of Al, Mo and C respectively, the alloy composition is Mg_2Cu_3Si. From the experimental results of Witte (1939), however, Mg_2Cu_3Si was found to be an ordered structure of *C*14 type ($MgZn_2$ structure). The *C*15-type ordered structure is stabilized only in the small region off the stoichiometric composition Mg_2Cu_3Si. The reason for this is left unresolved in the present study.

The long-range-order parameter defined after Warren (1969) is $S = \alpha_1 - \alpha_2$ even for such a non-stoichiometric composition; here α_1 and α_2 are occupancy factors for Cu atoms in sites 12(*d*) and 4(*a*), respectively. In the present specimen, the order parameter *S* was found to be 0·74 in contrast to $S = 0{\cdot}82$ for the expected highest-order parameter for this composition when site 12(*d*) is occupied entirely by Cu atoms.

Interatomic distances were calculated from the parameters obtained; they are given in Table 2, where only distances less than 3·5 Å are included. Coordination polyhedra around Mg atoms and small atoms (Cu, Si) are CN16 Friauf polyhedra (Samson, 1958) and CN12 icosahedra, respectively. Site 12(*d*) in the *C*15-type ordered structure is occupied by Cu atoms preferentially as in the case of site 6(*h*) in the *C*14-type ordered structure. Coordination polyhedra around Cu atoms of both structures are formed by six Mg, four Cu and two Si atoms. However, the scheme of the ordered arrangement of Si atoms in the *C*15-type ordered structure is different from that found in the *C*14-type ordered structure, as can be seen in Fig. 2. *C*14- and *C*15-type structures can be represented as two- and three-layer structures respectively, from the viewpoint of the Laves layers defined by Komura (1962). In the *C*14-type ordered structure, Cu atoms are located only on kagomé nets and Si atoms are only on triangular nets. On the other hand, in the *C*15-type ordered structure, Cu and Si atoms exist on both kinds of nets.

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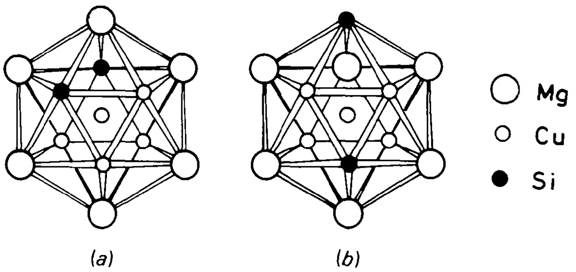
Table 2. *Interatomic distances* (Å) *in ordered* $Mg_{28.4}Cu_{57.9}Si_{13.7}$

Cu means the atom in site 12(*d*) and Si that in 4(*a*).

Mg	
Mg × 1	3·0908 (63)
Mg × 3	2·9882 (63)
Cu × 3	2·9016 (47)
Cu × 3	2·8795 (45)
Cu × 3	2·8565 (47)
Si × 3	2·9057 (45)

Cu	
Mg × 2	2·9016 (47)
Mg × 2	2·8795 (45)
Mg × 2	2·8565 (47)
Cu × 4	2·4903 (19)
Si × 2	2·4320 (11)

Si	
Mg × 6	2·9057 (45)
Cu × 6	2·4320 (11)



(*a*) (*b*)

Fig. 2. Coordination polyhedra around Cu atoms in (*a*) *C*15-type and (*b*) *C*14-type ordered structures.

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