density. Such a temperature effect would only be noticeable for elements with closely spaced partially occupied energy levels, like the 3*d* metals, but not for first- to third-row elements. This is consistent with the observation that the water densities are virtually identical at the two temperatures. If the above interpretation is correct it is, to our knowledge, the first time a temperature effect in the occupation of the electronic energy levels has been detected by diffraction methods. This effect will be further studied quantitatively by refinement of the occupation factors of the energy levels at 25 K and RT.

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Structure Refinement of Mg_2Cu and a Comparison of the Mg_2Cu, Mg_2Ni and Al_2Cu Structure Types

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Abstract

Dimagnesium copper, Mg_2Cu, $M_r = 112.170$, orthorhombic, *Fddd* (70), $a = 5.275$ (1), $b = 9.044$ (1), $c = 18.328$ (2) Å, $V = 874.3$ (2) Å^3, $Z = 16$, $D_x = 3.41$ g cm^{-3}, Mo $K\alpha$ ($\lambda = 0.71073$ Å), $\mu = 101.145$ cm^{-1}, $F(000) = 848$, $T = 293$ K, $R = 0.034$ ($wR = 0.031$) for 17 refined parameters and 310 observed X-ray single-crystal reflections [$F_o > 3\sigma(F_o)$]. The refined parameters are consistent with the nonrefined parameters reported by Schubert & Anderko [*Z. Metallkd.* (1951), **42**, 321–325]. The Mg_2Cu structure type can be derived by a stacking of slabs that build up the Al_2Cu and Mg_2Ni structure types.

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Introduction

Magnesium-rich transition-metal alloys are of interest for hydrogen-storage applications (Schlapbach, 1988). Copper-based Mg_2Cu is one of these compounds, although it has not yet been found to form a stable ternary hydride under ambient conditions (Reilly & Wiswall, 1967). Its orthorhombic structure was determined by Ekwall & Westgren (1940) and later by Schubert & Anderko (1951) but the atomic parameters stated were not refined. In this paper we report atomic parameters as refined from single-crystal X-ray diffraction and discuss the structural relationship between the Mg_2Cu, Mg_2Ni and Al_2Cu structure types.

Table 1. *Atomic coordinates and equivalent isotropic displacement parameters* U_{eq} ($Å^2$) *of* Mg_2Cu, *space group Fddd (No. 70)*

Estimated standard deviations are given in parentheses. $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	Site	x	y	z	U_{eq}
Mg(1)	16(*g*)	0.125	0.125	0.0415 (1)	0.0116 (6)
Mg(2)	16(*f*)	0.125	0.4586 (3)	0.125	0.0130 (6)
Cu	16(*g*)	0.125	0.125	0.49819 (4)	0.0104 (2)

Table 2. *Interatomic distances* (Å) *in* Mg_2Cu

Estimated standard deviations are given in parentheses.

Mg(1)—2Mg(1)	3.026 (2)	Mg(2)—2Mg(1)	3.383 (2)
— Mg(1)	3.063 (3)	—4Mg(1)	3.401 (1)
—2Mg(2)	3.383 (2)	—2Mg(1)	3.408 (2)
—4Mg(2)	3.401 (1)	—Mg(2)	3.010 (3)
—2Mg(2)	3.408 (2)	—2Mg(2)	3.040 (2)
—2Cu	2.7164 (7)	—2Cu	2.7218 (9)
—2Cu	2.7540 (7)	—2Cu	2.769 (1)
Cu—2Mg(1)	2.7164 (7)		
—2Mg(1)	2.7540 (7)		
—2Mg(2)	2.7218 (9)		
—2Mg(2)	2.769 (1)		
—2Cu	2.6182 (3)		

Experimental and results

The Mg_2Cu alloy was obtained from Ergenics [code name: HY-STOR 302; Huston & Sandrock (1980)]. A single crystal with approximate dimensions 0.05 × 0.07 × 0.15 mm was selected and measured at 293 K on an Enraf–Nonius CAD-4 automated four-circle diffractometer by using graphite-monochromatized Mo $K\alpha$ radiation.

The cell parameters (see *Abstract*) were refined from 25 centred reflections in the range $20.0 < 2\theta < 36.2°$. They were consistent with those reported by Schubert & Anderko (1951) ($a = 5.284$, $b = 9.07$, $c = 18.25$ Å). Integrated intensities for 385 unique reflections were collected out to $\sin\theta/\lambda = 0.746$ $Å^{-1}$ with $0 \le h \le 7$, $0 \le k \le 13$, $0 \le l \le 27$ in the ω–2θ scan mode. Three standard reflections were monitored periodically but no significant variation was observed. The systematic extinctions pointed to the space group *Fddd*, No. 70 (*International Tables for Crystallography*, 1983, Vol. A). The atomic scattering factors were taken from the *International Tables for X-ray Crystallography* (1974, Vol. IV). The structure refinement was based on F_o using the program *XTAL*3.0 (Hall & Stewart, 1990). The atomic coordinates found by Schubert & Anderko (1951) were standardized with the program *STRUCTURE TIDY* (Gelato & Parthé, 1987) and taken as a starting model for the refinement. 17 parameters (atoms with anisotropic displacement parameters) were refined to $R = 0.034$ [$wR = 0.031$, $S = 1.950$; $w = 1/\sigma^2(F_o)$] using 310 observed [$F_o > 3\sigma(F_o)$] of 385 measured reflections, no absorption correction, primary extinction coefficient $\rho = 0.034$ (6), maximum shift/e.s.d. in the last cycle 0.0003, residual electron density -0.9 e $Å^{-3}$ and $+1.3$ e $Å^{-3}$. Fractional atomic coordinates and isotropic displacement parameters are given in Table 1* and interatomic distances are presented in Table 2.

Discussion

The structural relationship between Mg_2Cu, Mg_2Ni and Al_2Cu was first recognized by Schubert (1964) and later also by Kripyakevich (1977), but was not described in detail. As shown in Fig. 1 all three structure types are built up by square antiprisms of

* Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55513 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU0325]

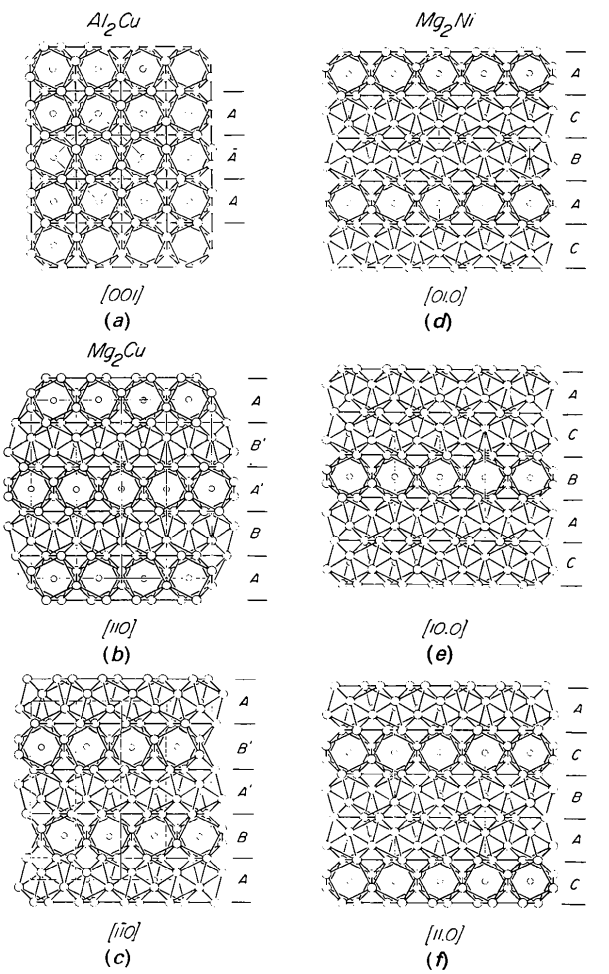

Fig. 1. The structures of (*a*) tetragonal Al_2Cu along [001]; orthorhombic Mg_2Cu along (*b*) [110] and (*c*) [1$\bar{1}$0]; and hexagonal Mg_2Ni along (*d*) [01.0], (*e*) [10.0] and (*f*) [11.0].

magnesium or aluminium atoms that are centred by transition-metal atoms. The antiprisms are connected *via* square faces to columns and these columns are connected *via* prism edges to slabs [see, for example, slabs marked *A* in Figs. 1(*a*), 1(*b*) and 1(*d*)].

The three structure types can be derived by various stackings of these slabs as follows. Consider the schematic representation of one such slab as shown in Fig. 2. The two parallel hexagonal nets indicate the edges of the square antiprisms of Al or Mg atoms that can be shared with the corresponding edges of neighbouring slabs below and above. Since these nets are displaced with respect to each other parallel to the net planes, neighbouring slabs must be shifted along the direction of the Cu or Ni atom rows by the height of one square antiprism to be superposable. This leads to the first and most simple of three possible ways of stacking, which is realized in the tetragonal Al_2Cu structure type [for a recent structure refinement see Meetsma, de Boer & van Smaalen (1989)]. Its unit cell contains two slabs. The stacking occurs along the [110] direction and can be denoted by the sequence $A\bar{A}A$ (Fig. 1*a*). The prism columns of all slabs are parallel to [001].

The second way of stacking is to rotate the previously shifted slabs against each other about the centre of a shared six-membered ring by about 60°. Successive operations of this type, with the sense of rotation changing, lead to the orthorhombic Mg_2Cu structure type. Its unit cell consists of four slabs that are stacked along the [001] direction in the sequence denoted $ABA'B'A$ (Figs. 1*b*, 1*c*). The in-plane orientations of the slabs alternate between the orthorhombic directions [110] (slabs *A* and *A'* in Fig. 1*b*) and [1$\bar{1}$0] (slabs *B* and *B'* in Fig. 1*c*). The angle between the prism columns in neighbouring slabs is 60.5°.

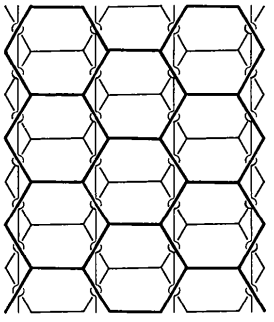

Fig. 2. Schematic representation of the structure slab building up the Al_2Cu, Mg_2Cu and Mg_2Ni structure types. The hexagonal nets indicate edges of square antiprisms of Al or Mg atoms that can be shared with those of the neighbouring slabs below (thin lines) and above (thick lines). Rows of open circles indicate Cu or Ni atoms that centre chains of square antiprisms.

The third way of stacking is identical to that before except that the sense of rotation after each translation is kept constant. This leads to the hexagonal Mg_2Ni structure type [for a recent structure refinement see Schefer *et al.* (1980)]. Its unit cell consists of a stacking of three slabs in the sequence denoted *ABCA* (Figs. 1*d*–1*f*). The in-plane orientations of the slabs alternate between the directions [01.0] (slab *A* in Fig. 1*d*), [10.0] (slab *B* in Fig. 1*e*) and [11.0] (slab *C* in Fig. 1*f*), *i.e.* neighbouring slabs are rotated by exactly 60° with respect to each other about the *c* axis.

Finally, it is worth pointing out that the Mg_2Cu structure type is rarely observed compared to the frequently observed Al_2Cu structure type (Havinga, Damsma & Hokkeling, 1972; Havinga, 1972; Havinga & Damsma, 1972), while no other representative has so far been reported for the Mg_2Ni structure type (Villars & Calvert, 1985). These different abundances could be the result of the different degrees of complexity of the structure stacking.

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