

of the three water molecules, there is no profit in attempting to unravel a detailed hydrogen-bonding scheme. There are many N...O and H₂O...O distances in the range 2.8–3.1 Å; the shortest, at 2.64 Å, is to an O atom of group S(3) and hence has a large and unspecified uncertainty.

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Ca₂Cu with Trigonal-Prismatic Coordination of the Copper Atoms Forming Infinite Chains

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Abstract. Ca₂Cu, orthorhombic, *Pnma*, $a = 6.126$ (2), $b = 4.161$ (4), $c = 14.53$ (1) Å, $Z = 4$, $D_c = 2.58$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 8.4$ mm⁻¹. The structure was solved by direct methods and refined isotropically to an R value of 0.082 for 118 reflexions. The structure of Ca₂Cu is built up by stacking Cu-centered trigonal prisms of Ca atoms in such a way that they share two rectangular faces. This arrangement allows infinite zigzag chains of Cu atoms to be formed, giving a close relationship with the FeB-type structure.

Introduction. In the phase diagram studied by Bruzzone (1971) three phases exist: CaCu₅ with its own well known structure, CaCu present in two modifications [both stacking variants of the FeB–CrB types (Merlo & Fornasini, 1981)], and Ca₂Cu with unknown structure. The purpose of this work was to determine the crystal structure of this last phase.

In order to avoid the formation of the more stable compound CaCu, an alloy of nominal composition 7Ca:3Cu was prepared by melting the two metals (Ca 99.9, Cu 99.999% purity) in an iron crucible and annealing at 723 K for two months.

The softness and oxidizability of the alloy prevented good crystals being easily found; their diffraction spots were in every case elongated and intensities dropped at high θ values. After many trials a plate-like single crystal of acceptable quality and dimensions 0.02 × 0.06 × 0.17 mm was chosen for the X-ray analysis.

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Precession photographs showed orthorhombic symmetry with $0kl$ reflexions present only for $k + l = 2n$ and $hk0$ present only for $h = 2n$, indicating space groups *Pn2₁a* and *Pnma*.

The crystal was then mounted on an Enraf–Nonius CAD-4 automatic diffractometer and 1212 hkl reflexions were measured with graphite-monochromated Mo $K\alpha$ radiation in the ω – 2θ scan mode ($3 \leq \theta \leq 30^\circ$). A check reflexion was employed to test the stability of the crystal; this faded at the end of the data collection. A decay correction, as a function of the elapsed time, was then applied, together with Lorentz and polarization corrections. Absorption was taken into account using the semi-empirical method of North, Phillips & Mathews (1968) with 18 ψ -scan data of a strong reflexion. Finally, averaging gave 609 independent reflexions.

The lattice constants were obtained from a least-squares refinement of 24 diffractometer-measured reflexions, and by comparing the cell volume with that calculated using the elemental atomic volumes, four Ca₂Cu formulae per cell could be assigned.

For the structure resolution and refinement the *SHELX 76* program (Sheldrick, 1976) was used, taking atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Direct methods in the space group *Pnma* gave a solution compatible with both cell content and geometrical requirements. An

Table 1. Atomic parameters for Ca₂Cu (space group *Pnma*), with e.s.d.'s in parentheses

The thermal factors are defined as $\exp[-8\pi^2 U(\sin \theta/\lambda)^2]$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å ²)
Ca(1)	0.363 (3)	0.25	0.6669 (9)	0.020 (5)
Ca(2)	0.134 (3)	0.25	0.4070 (8)	0.013 (4)
Cu	0.109 (2)	0.25	0.0147 (5)	0.011 (3)

isotropic least-squares refinement of ten parameters was made for 118 reflexions with $F_o > 2\sigma(F_o)$ and $w = 1/\sigma^2(F_o)$, and converged to an *R* value of 0.082. The final atomic parameters are listed in Table 1.*

Discussion. In the structure of Ca₂Cu (Fig. 1a) the Ca atoms form slabs of trigonal prisms alternately inclined $\pm 19^\circ$ about the *c* axis. The prisms share two rectangular faces with two other prisms, originating rows in the [010] direction, and are centered by Cu atoms which form infinite zigzag chains in the same direction.

This structure can be related to that of the FeB type (Fig. 1b); if alternate slabs of trigonal prisms are translated *b*/2 and then joined together by shifting along the *c* axis, the atomic arrangement of the FeB structure is derived. Such a connexion is not surprising, as stacking variants of the FeB–CrB types exist for the two modifications, α and β , of the phase CaCu (Merlo & Fornasini, 1981), which show features very similar to those of the Ca₂Cu structure. Indeed, the prism inclination angle, the prism dimensions and the coordination around the Cu atoms are practically the same in the three structures. Cu always has six Ca neighbors at the vertices of a trigonal prism, while a seventh Ca and two Cu atoms capping the rectangular faces complete the coordination.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36796 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

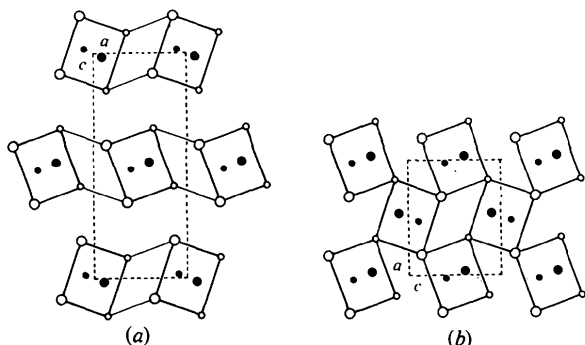


Fig. 1. Projection of (a) the Ca₂Cu and (b) the FeB structures along the short axis. Open circles: Ca or Fe; full circles: Cu or B. Large circles are in the plane of the sheet, small circles are above and below the plane of the sheet. Trigonal prisms are indicated by thick lines.

Table 2. Interatomic distances (Å) in Ca₂Cu

E.s.d.'s are given in parentheses.

Ca(1)–1Cu	3.04 (2)	Cu–2Cu	2.51 (1)
–2Cu	3.04 (1)	–1Ca(1)	3.04 (2)
–2Ca(2)	3.84 (2)	–2Ca(1)	3.04 (1)
–2Ca(2)	3.87 (2)	–2Ca(2)	3.04 (1)
–2Ca(1)	3.90 (2)	–1Ca(2)	3.12 (2)
–1Ca(2)	4.03 (2)	–1Ca(2)	3.41 (2)
–2Ca(2)	4.06 (2)		
–2Ca(1)	4.16 (1)		
Ca(2)–2Cu	3.04 (1)	Ca(2)–2Ca(1)	3.87 (2)
–1Cu	3.12 (2)	–1Ca(1)	4.03 (2)
–1Cu	3.41 (2)	–2Ca(1)	4.06 (2)
–2Ca(2)	3.79 (2)	–2Ca(2)	4.16 (1)
–2Ca(1)	3.84 (2)		

As can be seen in Table 2, interatomic distances in Ca₂Cu are also very close to those of α - and β -CaCu, having a maximum contraction (6%) with respect to the sum of the metallic radii in the Ca–Cu distances within the prism. However, the volume contraction, calculated on the basis of the elemental atomic volumes for Ca₂Cu and for α - and β -CaCu, are 6.4, 11.7 and 11.9%, respectively, indicating on the whole a less dense space filling for the Ca₂Cu structure. In fact, the prism slabs, linked in the direction of the *c* axis only by Ca–Ca bonds, generate in between tetrahedral and octahedral holes, which are absent in FeB and in its stacking variants.

Interestingly, Ca₂Cu does not adopt the *anti*-PbCl₂-type structure, which occurs for several *M*₂*X* compounds of alkaline earths with Hg, Si, Ge, Sn and Pb, although it is also based on trigonal-prismatic coordination around the *X* atom. In spite of the same linkage coefficient, as defined by Parthé & Moreau (1977), which is 3 for both structures, the prism arrangement is quite different: in the *anti*-PbCl₂ type the prisms share their triangular faces to give columns, each column being connected to two other columns by sharing two lateral edges of the prisms. So, no *X*–*X* contact is allowable and the atom centering the prisms displays only hetero-atomic bonds. The possibility of Cu forming chains, as in the dimorphic CaCu phase, could explain why Ca₂Cu presents this new structure.

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