

The Structures of α -CaCu, β -CaCu, SrAg and BaAg: Four Different Stacking Variants Based on Noble-Metal-Centred Trigonal Prisms

BY FRANCO MERLO AND MARIA L. FORNASINI

Istituto di Chimica Fisica, Università di Genova, Corso Europa, Palazzo delle Scienze, 16132 Genova, Italy

(Received 21 July 1980; accepted 6 November 1980)

Abstract

α -CaCu [$a = 38.80$ (1), $b = 4.271$ (2), $c = 5.894$ (9) Å, $Z = 20$], SrAg [$a = 16.558$ (7), $b = 4.788$ (1), $c = 6.385$ (1) Å, $Z = 8$] and BaAg [$a = 8.657$ (3), $b = 4.982$ (3), $c = 6.651$ (3) Å, $Z = 4$] crystallize in the same space group, $Pnma$. β -CaCu [$a = 19.47$ (1), $b = 4.271$ (2), $c = 5.880$ (3) Å, $\beta = 94.3$ (1)°, $Z = 10$] crystallizes in $P2_1/m$. The structures were solved with the aid of starting models and refined with isotropic temperature factors, using photographic data, for α -CaCu (171 reflexions, $R = 0.061$), β -CaCu (360 reflexions, $R = 0.095$) and BaAg (85 reflexions, $R = 0.095$); refinements with anisotropic temperature factors were carried out for SrAg (638 reflexions, $R = 0.053$) with data measured on a single-crystal diffractometer. BaAg belongs to the FeB structure type, whilst α -CaCu, β -CaCu and SrAg represent new examples of stacking variants of the CrB–FeB types. The four structures are based on the same trigonal-prismatic coordination around the noble metals and differ only in the arrangement and sequence of the prisms along the a axis.

Introduction

In a previous paper we report the results obtained for the phases SrCu and BaCu (Fornasini & Merlo, 1980). Now, continuing our study of the equiatomic compounds formed by the alkaline-earth elements with Cu, Ag and Au, the crystal structures of CaCu, SrAg and BaAg have been investigated.

In the binary equilibrium diagrams Ca–Cu (Bruzzone, 1971) and Sr–Ag (Weibke, 1930) the existence of the corresponding equiatomic phases is reported. CaCu melts peritectically at 840 K; SrAg melts congruently at 953 K. No data are available for BaAg.

Experimental

The metals used were calcium, strontium and barium from Fluka Co. (Switzerland) of 99.9, 99.5 and 99.5

wt % purity, respectively, and copper and silver from Koch–Light (England) of 99.999 wt % purity. The alloys were prepared by melting stoichiometric amounts of the two metals in iron crucibles (CaCu) and in tantalum containers (SrAg and BaAg) sealed under argon. BaAg was further annealed for a month at 773 K. Owing to their high oxidizability, the alloys had to be handled in an argon atmosphere and crushed under paraffin oil; the crystals were sealed in thin glass capillaries under vacuum. Single crystals were examined by Weissenberg and precession techniques.

A few words must be said concerning CaCu. A sample of CaCu was conventionally prepared, in accordance with the phase-diagram data, by melting and slowly cooling the alloy. Whilst most single crystals showed reflexions of a phase later identified as the monoclinic β -CaCu, some crystals from the same matrix presented in addition other weak reflexions. In order to clarify the situation, two alloys were prepared, and each was subjected to a different thermal treatment. The first was melted and quenched from 873 K in water: the crystals examined belonged to an orthorhombic modification (α -CaCu). The second was melted and annealed at 643 K for three months: the crystals examined corresponded to the β -CaCu monoclinic modification. Though no thermal effects were observed in a differential-thermal-analysis curve, the stability of the two polymorphs is related to the temperature; so, α - and β -CaCu can be regarded as the high- and low-temperature modifications, respectively. The very pronounced twinning observed for most β -CaCu crystals can be ascribed to the special lattice dimensions of this phase ($a^2:b^2:c^2:ac \cos \beta^* \simeq 44:2:4:1$).

The crystals of α -CaCu, SrAg and BaAg showed orthorhombic symmetry with the same systematic absences for $0kl$ reflexions with $k + l = 2n + 1$ and for $hk0$ with $h = 2n + 1$, indicating $Pn2_1a$ and $Pnma$ as possible space groups. The β -CaCu phase showed monoclinic symmetry with systematic absences for $0k0$ with $k = 2n + 1$, indicating $P2_1$ and $P2_1/m$ as possible space groups. Owing to the occurrence of only two layers of atoms along the b axis (as established later), in both cases the centrosymmetric space group was adopted.

The lattice constants were derived from precession photographs using a least-squares procedure. For SrAg the lattice constants were determined from least-squares refinement of 52 diffractometer-measured reflexions.

Intensities of reflexions of α -CaCu and β -CaCu were collected on integrated Weissenberg photographs taken with Cu $K\alpha$ radiation; those of BaAg were collected on integrated precession photographs taken with Mo $K\alpha$ radiation. The intensities were measured with a microdensitometer and corrected for the background by subtracting the mean value of four readings around each spot. Lorentz, polarization and absorption corrections were applied and equivalent reflexions averaged, giving 171, 360 and 85 independent reflexions for α -CaCu, β -CaCu and BaAg, respectively.

In the case of SrAg, the intensities of 1999 reflexions were recorded on a four-circle automatic diffractometer with graphite-monochromated Mo $K\alpha$ radiation up to $\theta = 30^\circ$ in the ω -scan mode, with a scan width of 3° , measuring at least two symmetry-related reflexions. The data were corrected for Lorentz, polarization and absorption effects, applying the semi-empirical method of North, Phillips & Mathews (1968), by the use of 36 ψ -scan values. After correction, the discrepancy index among equivalent reflexions was 3.3% and averaging gave 819 independent reflexions.

The *SHELX 76* system of programs (Sheldrick, 1976) was employed in the structure refinement with the full-matrix least-squares procedure. Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974).

Structure determination

α -CaCu and β -CaCu

The symmetry and lattice constants of these compounds, related to those of YbCu (FeB type, $a = 7.568$, $b = 4.260$, $c = 5.771$ Å, space group *Pnma*; Iandelli & Palenzona, 1971), and the intensity distribution, which presents a large number of unobserved reflexions, suggested that their structures might be different stacking variations of the CrB–FeB structure types, analogous to those found by Lemaire & Paccard (1970) in dimorphic TbNi and by Klepp & Parthé (1980) in the quasi-binary systems GdNi–YNi and GdNi–DyNi. Moreover, following the methods given by Klepp & Parthé for the construction of a starting model, we were able to propose for each modification the atomic arrangements in accordance with cell sizes and symmetry requirements.

Out of the three possible orthorhombic structures compatible with the space group *Pnma*, one provided

intensities in good agreement with the observed values for α -CaCu. For β -CaCu two monoclinic models were derived in the space group *P2₁/m* and one was found to be correct.

Isotropic refinement of the two structures, with unit weights, was made, obtaining at convergence final *R* values of 0.061 for α -CaCu (171 reflexions) and 0.095 for β -CaCu (360 reflexions).

SrAg

Analogous considerations hold in the case of SrAg, where the lattice constant *a* is twice the corresponding value in the FeB type. A stacking variation, again based on the CrB–FeB structures, was univocally proposed in the space group *Pnma* and confirmed to be the correct one. Isotropic refinement was accomplished with weights $w = 1/\sigma^2(F_o)$ over the 638 reflexions having $|F_o| > \sigma(F_o)$. In fact, with this low limit the rejected reflexions represent 22% of the total number. At convergence the conventional *R* index was 0.063. Two further cycles with anisotropic temperature factors lowered *R* to 0.053.

The phase ThNi is known to exist with its own structure type (Florio, Baenziger & Rundle, 1956). This compound has the same space group and number of atoms per cell as SrAg and very similar *c/b* and *a/c* lattice-constant ratios, but different atomic positions and coordination. A sample of ThNi was then prepared, and the program *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977) was used to calculate powder intensities, both on the basis of the atomic parameters of Florio *et al.* (1956) and those of the SrAg structure. The observed powder-pattern intensities were found to agree better with the SrAg-type model and a single-crystal determination is in progress to refine the structure of ThNi.

BaAg

This phase was found to crystallize with the FeB structure type. Refinement of positional and isotropic thermal parameters using the 85 measured reflexions, with unit weights, led to an *R* of 0.095.

Table 1 collects the structural data of the four examined structures.*

Discussion

Fig. 1 shows the elementary cell and some geometrical features common to the four structures. In each case

* Lists of structure factors and, for SrAg, anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35717 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Structural data for α -CaCu, β -CaCu, SrAg and BaAg*

All positions have $y = \frac{1}{2}$. The thermal parameters are defined as $\exp[-8\pi^2 U(\sin \theta/\lambda)^2]$. For SrAg the isotropic U 's are derived from the anisotropic values by $U = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

α -CaCu				β -CaCu				SrAg			
$\mu(\text{Cu } K\alpha) = 33.5 \text{ mm}^{-1}$, crystal size: $0.09 \times 0.09 \times 0.17 \text{ mm}$, $R = 0.061$				$\mu(\text{Cu } K\alpha) = 33.5 \text{ mm}^{-1}$, crystal size: $0.10 \times 0.13 \times 0.35 \text{ mm}$, $R = 0.095$				$\mu(\text{Mo } K\alpha) = 29.1 \text{ mm}^{-1}$, crystal size: $0.02 \times 0.06 \times 0.38 \text{ mm}$, $R = 0.053$ (anisotropic refinement)			
	x	z	$U (\text{\AA}^2)$		x	z	$U (\text{\AA}^2)$		x	y	$U (\text{\AA}^2)$
Ca(1)	0.4638 (4)	0.6321 (26)	0.020 (1)	Ca(1)	0.1276 (5)	0.6550 (14)	0.012 (2)	Sr(1)	0.2851 (1)	0.5127 (2)	0.0170 (7)
Ca(2)	0.3652 (5)	0.8735 (24)	0.020 (1)	Ca(2)	0.3281 (5)	0.4626 (14)	0.013 (2)	Sr(2)	0.0349 (1)	0.7467 (2)	0.0164 (6)
Ca(3)	0.2639 (4)	0.1259 (26)	0.020 (1)	Ca(3)	0.5285 (4)	0.7576 (14)	0.009 (2)	Ag(1)	0.3574 (1)	0.0027 (2)	0.0186 (6)
Ca(4)	0.1644 (5)	0.8726 (24)	0.020 (1)	Ca(4)	0.7279 (5)	0.0515 (14)	0.014 (2)	Ag(2)	0.1078 (1)	0.2570 (2)	0.0190 (5)
Ca(5)	0.0649 (5)	0.6362 (25)	0.020 (1)	Ca(5)	0.9290 (4)	0.8565 (14)	0.011 (2)	BaAg			
Cu(1)	0.0931 (3)	0.1010 (20)	0.021 (1)	Cu(1)	0.1882 (3)	0.1913 (10)	0.013 (2)	$\mu(\text{Mo } K\alpha) = 20.3 \text{ mm}^{-1}$, crystal size: $0.02 \times 0.07 \times 0.16 \text{ mm}$, $R = 0.095$			
Cu(2)	0.1948 (3)	0.3503 (18)	0.021 (1)	Cu(2)	0.3882 (3)	0.9528 (10)	0.011 (2)		x	y	$U (\text{\AA}^2)$
Cu(3)	0.2938 (3)	0.6441 (18)	0.021 (1)	Cu(3)	0.5882 (3)	0.2499 (10)	0.008 (1)	Ba	0.180 (1)	0.129 (2)	0.022 (3)
Cu(4)	0.3934 (3)	0.3943 (19)	0.021 (1)	Cu(4)	0.7876 (3)	0.5894 (10)	0.013 (2)	Ag	0.033 (1)	0.631 (3)	0.020 (4)
Cu(5)	0.4940 (3)	0.1072 (20)	0.021 (1)	Cu(5)	0.9871 (3)	0.3890 (10)	0.014 (2)				

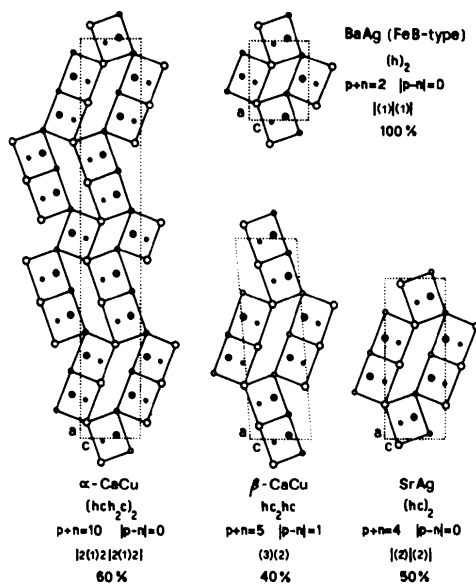


Fig. 1. Projection of the structure of each examined phase along the b axis illustrating the trigonal prisms, which are indicated by solid lines. Open circles: alkaline-earth atoms; full circles: Cu or Ag atoms. Large circles are in the plane of the sheet, small circles are above and below the plane of the sheet. Dotted lines indicate the cell edges. For notations below each drawing, see text.

the noble metals are coordinated by six alkaline-earth atoms at the vertices of trigonal prisms, which are indicated in the figure by solid lines. The lateral faces of the trigonal prisms are capped by another alkaline earth and by two noble metals, the copper or silver atoms forming selenium-like zigzag chains.

As already remarked by Hohnke & Parthé (1966), Lemaire & Paccard (1970) and Parthé (1976), the CrB and FeB types have to be considered the simplest members of a structural family based on the trigonal-prismatic coordination. Indeed, an infinite number of

stacking variations can be built up using different fragments of both these structures, always maintaining the trigonal prism as the common unit. Some of them have already been found in the low- and high-temperature forms of TbNi (Lemaire & Paccard, 1970) and in the quasi-binary systems GdNi–YNi and GdNi–DyNi (Klepp & Parthé, 1980); the structures of α -CaCu, β -CaCu and SrAg represent new examples.

In order to give a homogeneous description of these types of structure, it is useful to employ the criteria of identification of Klepp & Parthé (1980), recently developed by the same authors in the classification of the stacking variants up to ten layers (Klepp & Parthé, 1981). They are: (i) the Jagodzinski notation, connected with the interpretation of trigonal-prism-based structures in terms of the microtwinning mechanism (Parthé, 1976); (ii) $p + n$, $|p - n|$, where p and n are the total numbers of prisms in each of the two possible orientations along the a axis; (iii) the Zhdanov symbol, formed by digits representing the sequence of iso-oriented prisms; (iv) the percentage of hexagonal stacking.

These notations, which follow and extend those used for the stacking of close-packed layers (*International Tables for X-ray Crystallography*, 1967), are reported in Fig. 1 under each drawing.

Interatomic distances for the four structures, given in Table 2, are quite normal compared with the sums of the metallic radii. The shortest distances occur between the noble-metal and the alkaline-earth atoms belonging to the prisms, with contractions which do not exceed 9% in any case. Moreover, although atoms of the same element occupy more than one crystallographic site, they present the same coordination polyhedra, with some slight differences in the distances.

In conclusion, these facts confirm the similarities amongst the CrB–FeB stacking variants not only from a geometrical viewpoint, but also from a chemical one:

Table 2. *Interatomic distances (Å) in α -CaCu, β -CaCu, SrAg and BaAg*The e.s.d.'s are less than 0.03 Å for α -CaCu, β -CaCu and BaAg, and less than 0.01 Å for SrAg. α -CaCu

Ca(1) - 2 Ca(5) 3.79	Ca(4) - 2 Ca(3) 3.80	Cu(2) - 2 Cu(3) 2.50
- 2 Ca(5) 3.82	- 2 Ca(2) 3.81	- 1 Ca(3) 2.99
- 2 Ca(1) 3.86	- 2 Ca(2) 3.82	- 1 Ca(4) 3.05
- 1 Ca(2) 4.08	- 1 Ca(5) 4.10	- 2 Ca(3) 3.13
- 1 Ca(5) 4.15	- 1 Ca(3) 4.14	- 2 Ca(2) 3.16
- 2 Ca(1) 4.27	- 2 Ca(4) 4.27	- 1 Ca(4) 3.30
- 1 Cu(5) 3.04	- 1 Cu(2) 3.05	
- 1 Cu(4) 3.07	- 1 Cu(1) 3.08	Cu(3) - 2 Cu(2) 2.50
- 2 Cu(1) 3.08	- 2 Cu(4) 3.10	- 1 Ca(3) 3.07
- 2 Cu(5) 3.10	- 2 Cu(3) 3.12	- 1 Ca(2) 3.08
- 1 Cu(5) 3.31	- 1 Cu(2) 3.30	- 2 Ca(3) 3.10
		- 2 Ca(4) 3.12
		- 1 Ca(3) 3.27
Ca(2) - 2 Ca(5) 3.78	Ca(5) - 2 Ca(2) 3.78	Cu(4) - 2 Cu(1) 2.51
- 2 Ca(4) 3.81	- 2 Ca(1) 3.79	- 1 Ca(2) 3.03
- 2 Ca(4) 3.82	- 2 Ca(1) 3.82	- 1 Ca(1) 3.07
- 1 Ca(1) 4.08	- 1 Ca(4) 4.10	- 2 Ca(5) 3.08
- 1 Ca(3) 4.20	- 1 Ca(1) 4.15	- 2 Ca(4) 3.10
- 2 Ca(2) 4.27	- 2 Ca(5) 4.27	- 1 Ca(2) 3.26
- 1 Cu(4) 3.03	- 1 Cu(1) 2.95	
- 1 Cu(3) 3.08	- 2 Cu(4) 3.08	Cu(5) - 2 Cu(5) 2.52
- 2 Cu(1) 3.12	- 1 Cu(5) 3.10	- 1 Ca(1) 3.04
- 2 Cu(2) 3.16	- 2 Cu(5) 3.13	- 2 Ca(1) 3.10
- 1 Cu(4) 3.26	- 1 Cu(1) 3.34	- 1 Ca(5) 3.10
		- 2 Ca(5) 3.13
		- 1 Ca(1) 3.31
Ca(3) - 4 Ca(3) 3.80	Cu(1) - 2 Cu(4) 2.51	
- 2 Ca(4) 3.80	- 1 Ca(5) 2.95	
- 1 Ca(4) 4.14	- 2 Ca(1) 3.08	
- 1 Ca(2) 4.20	- 1 Ca(4) 3.08	
- 2 Ca(3) 4.27	- 2 Ca(2) 3.12	
- 1 Cu(2) 2.99	- 1 Ca(5) 3.34	
- 1 Cu(3) 3.07		
- 2 Cu(3) 3.10		
- 2 Cu(2) 3.13		
- 1 Cu(3) 3.27		

 β -CaCu

Ca(1) - 2 Ca(5) 3.78	Ca(4) - 2 Ca(2) 3.79	Cu(2) - 2 Cu(3) 2.50
- 2 Ca(5) 3.81	- 2 Ca(2) 3.79	- 1 Ca(2) 3.03
- 2 Ca(4) 3.84	- 2 Ca(1) 3.84	- 1 Ca(3) 3.04
- 1 Ca(5) 4.13	- 1 Ca(3) 4.13	- 2 Ca(4) 3.11
- 1 Ca(2) 4.15	- 1 Ca(5) 4.16	- 2 Ca(3) 3.11
- 2 Ca(1) 4.27	- 2 Ca(4) 4.27	- 1 Ca(2) 3.30
- 1 Cu(5) 3.05	- 1 Cu(4) 3.03	
- 1 Cu(1) 3.05	- 1 Cu(3) 3.04	Cu(3) - 2 Cu(2) 2.50
- 2 Cu(5) 3.09	- 2 Cu(1) 3.10	- 1 Ca(3) 3.04
- 2 Cu(4) 3.12	- 2 Cu(2) 3.11	- 1 Ca(4) 3.04
- 1 Cu(1) 3.28	- 1 Cu(4) 3.29	- 2 Ca(2) 3.11
		- 2 Ca(3) 3.12
		- 1 Ca(3) 3.28
Ca(2) - 2 Ca(4) 3.79	Ca(5) - 2 Ca(1) 3.78	Cu(4) - 2 Cu(1) 2.52
- 2 Ca(4) 3.79	- 2 Ca(5) 3.79	- 1 Ca(1) 4.13
- 2 Ca(3) 3.82	- 2 Ca(1) 3.81	- 1 Ca(4) 4.16
- 1 Ca(1) 4.15	- 1 Ca(1) 4.13	- 2 Ca(2) 3.10
- 1 Ca(3) 4.15	- 1 Ca(4) 4.16	- 2 Ca(1) 3.12
- 2 Ca(2) 4.27	- 2 Ca(5) 4.27	- 1 Ca(4) 3.29
- 1 Cu(2) 3.03	- 1 Cu(5) 3.05	
- 1 Cu(1) 3.05	- 1 Cu(4) 3.07	
- 2 Cu(4) 3.10	- 2 Cu(5) 3.11	
- 2 Cu(3) 3.11	- 2 Cu(1) 3.12	Cu(5) - 2 Cu(5) 2.53
- 1 Cu(2) 3.30	- 1 Cu(5) 3.25	- 1 Ca(1) 3.05
		- 1 Ca(5) 3.05
Ca(3) - 2 Ca(3) 3.79	Cu(1) - 2 Cu(4) 2.52	- 2 Ca(1) 3.09
- 2 Ca(3) 3.80	- 2 Ca(1) 3.05	- 2 Ca(5) 3.11
- 2 Ca(2) 3.82	- 1 Ca(2) 3.05	- 1 Ca(5) 3.25
- 1 Ca(4) 4.13	- 2 Ca(4) 3.10	
- 1 Ca(2) 4.15	- 2 Ca(5) 3.12	
- 2 Ca(3) 4.27	- 1 Ca(1) 3.28	
- 1 Cu(3) 3.04		
- 1 Cu(2) 3.04		
- 2 Cu(2) 3.11		
- 2 Cu(3) 3.12		
- 1 Cu(3) 3.28		

SrAg

Sr(1) - 4 Sr(1) 4.16	Sr(2) - 2 Sr(2) 4.12	Ag(1) - 2 Ag(2) 2.92
- 2 Sr(2) 4.18	- 2 Sr(1) 4.18	- 1 Sr(2) 3.34
- 1 Sr(2) 4.40	- 2 Sr(2) 4.19	- 1 Sr(1) 3.35
- 1 Sr(2) 4.41	- 1 Sr(1) 4.40	- 2 Sr(1) 3.36
- 2 Sr(1) 4.79	- 1 Sr(1) 4.41	- 2 Sr(2) 3.37
- 1 Ag(1) 3.35	- 2 Sr(2) 4.79	- 1 Sr(1) 3.47
- 1 Ag(2) 3.36	- 1 Ag(1) 3.34	
- 2 Ag(1) 3.36	- 1 Ag(2) 3.35	
- 2 Ag(2) 3.36	- 2 Ag(2) 3.36	
- 1 Ag(1) 3.47	- 2 Ag(1) 3.37	
	- 1 Ag(2) 3.47	

BaAg

Ag(2) - 2 Ag(1) 2.92	Ba - 4 Ba 4.33	Ag - 2 Ag 3.09
- 1 Sr(2) 3.35	- 2 Ba 4.34	- 2 Ba 3.49
- 1 Sr(1) 3.36	- 2 Ba 4.62	- 1 Ba 3.51
- 2 Sr(1) 3.36	- 2 Ba 4.98	- 2 Ba 3.52
- 2 Sr(2) 3.36	- 2 Ag 3.49	- 1 Ba 3.55
- 1 Sr(2) 3.47	- 1 Ag 3.51	- 1 Ba 3.57
	- 2 Ag 3.52	
	- 1 Ag 3.55	
	- 1 Ag 3.57	

the same heteroatomic bond factor is responsible for the presence of the trigonal prism as the common unit and controls the interaction of the nearest neighbours. On the other hand, since all these structures probably have very similar energies, it is difficult at present to establish the reason why a particular stacking sequence is adopted in a structure, not forgetting that long-range interactions can play an important role.

We wish to thank Professor A. Iandelli for his interest during the work, and the Centro di Cristallografia Strutturale del CNR (University of Pavia) for the collection of intensities of SrAg on the PW 1100 diffractometer.

References

- BRUZZONE, G. (1971). *J. Less-Common Met.* **25**, 361-366.
 FLORIO, J. V., BAENZIGER, N. C. & RUNDLE, R. E. (1956). *Acta Cryst.* **9**, 367-372.
 FORNASINI, M. L. & MERLO, F. (1980). *Acta Cryst.* **B36**, 1288-1291.
 HOHNKE, D. & PARTHÉ, E. (1966). *Acta Cryst.* **20**, 572-582.
 IANDELLI, A. & PALENZONA, A. (1971). *J. Less-Common Met.* **25**, 333-335.
International Tables for X-ray Crystallography (1967). Vol. II, ch. 7.1. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 KLEPP, K. & PARTHÉ, E. (1980). *Acta Cryst.* **B36**, 774-782.
 KLEPP, K. & PARTHÉ, E. (1981). *Acta Cryst.* **B37**, 495-499.
 LEMAIRE, R. & PACCARD, D. (1970). *J. Less-Common Met.* **21**, 403-413.
 NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351-359.
 PARTHÉ, E. (1976). *Acta Cryst.* **B32**, 2813-2818.
 SHELDRIK, G. M. (1976). *SHELX 76*. A program for crystal structure determination. Univ. of Cambridge, England.
 WEIBKE, F. (1930). *Z. Anorg. Chem.* **193**, 297-310.
 YVON, K., JEITSCHKO, W. & PARTHÉ, E. (1977). *J. Appl. Cryst.* **10**, 73-74.