

first approximation, a closest-packed sheet. The sequence of layers is *ABBA*..., but one of the two neighbouring *B* layers is translated by a vector ($a/2 + b/2$) with respect to the other, in such a way that each Ba(2) atom has a Bi atom as nearest neighbour on the adjacent layer of the same kind. The atoms of these *B* layers are not exactly coplanar. Each Ba(2) atom is shifted 0.68 Å from the plane built up by the Bi atoms in the direction of the adjacent *B* layer.

The Ba(1) atoms have 12 neighbours, 4Bi, 4Ba(1) and 4Ba(2) atoms at distances of 3.668, 3.722 and 4.173 Å, respectively. The Ba(2) atoms have nine neighbours, 1Bi, 4Bi and 4Ba(1) atoms at distances of 3.556, 3.784 and 4.173 Å, respectively. Additionally there are 4Ba(2) atoms of the adjacent *B* layer at distances appreciably greater (4.701 Å) which probably contribute to a smaller extent to the bonding. Each Bi atom is surrounded by nine barium atoms forming the unit BiBa₉, similar to the SbSr₉ units found in the isomorphous compound Sr₂Sb. The average of the Bi–Ba distances is 3.707 Å.

The Ba(1)–Ba(1) distances of 3.722 Å mentioned above are appreciably shorter than the minimum distance of 4.34 Å in metallic barium and probably indicate some ionic character of bonds.

A list of interatomic distances is given in Table 2.

Thanks are due to Huber Diffraktions-Technik for facilities to obtain the intensity data. Dr Müller kindly allowed us to use a sample used in the work for his Thesis. We are indebted to the Deutsche Forschungsgemeinschaft for financial support given to M.M.R.

Table 2. *Interatomic distances*

Estimated standard deviation ±0.008 Å.

Around Ba(1)		Around Ba(2)	
Ba(1)–Bi	3.668 Å (× 4)	Ba(2)–Bi	3.556 Å (× 1)
Ba(1)–Ba(1)	3.722 (× 4)	Ba(2)–Bi	3.784 (× 4)
Ba(1)–Ba(2)	4.173 (× 4)	Ba(2)–Ba(1)	4.173 (× 4)
		Ba(2)–Ba(2)	4.701 (× 4)
Around Bi		Averages	
Bi–Ba(2)	3.556 Å (× 1)	Ba(1)–Bi	3.668 Å
Bi–Ba(1)	3.668 (× 4)	Ba(1)–Ba	3.948
Bi–Ba(2)	3.784 (× 4)	Ba(2)–Bi	3.738
		Ba(2)–Ba	4.173
		Bi—Ba	3.707

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The Crystal Structure of Ca₅Bi₃

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Ca₅Bi₃ crystallizes in the orthorhombic system, space group *Pnma*, with 4 formula units in a cell of size $a = 12.722$ (8), $b = 9.666$ (6), $c = 8.432$ (6) Å. The calculated density is 5.298 g cm⁻³. These data compare with those given by Brauer & Müller [*Angew. Chem.* (1961). **73**, 169]: 12.74, 9.69, 8.46 Å and macroscopic density 5.21 g cm⁻³. Ca₅Bi₃ is isomorphous with Ca₅Sb₃.

Introduction

Single crystals of Ca₅Bi₃ can be prepared by a method similar to that described in the case of Ca₅Sb₃ (Martinez-Ripoll & Brauer, 1974). The crystals are black and have nearly prismatic shape, the *a* axis being parallel to the needle axis. Because of their extreme instability in air they had to be kept under argon atmosphere.

A prismatic single crystal with nearly circular cross section (0.16 mm diameter) was used mounted on a

Huber diffractometer (RHD 402) on-line to a PDP-8 computer. The intensity data from 16 reciprocal layers perpendicular to the *a* axis were obtained by using graphite-monochromated Mo *K*α radiation in connexion with a scintillation detector and pulse-height discrimination. 1378 reflexions were collected. Of this total, 1070 reflexions were considered 'observed' according to the criterion $I > 2\sigma(I)$ and used in the refinement. Absorption corrections ($\mu R = 4.04$) were made assuming cylindrical crystal shape. The intensities were

corrected for Lorentz and polarization effects in the usual manner.

Atomic coordinates and isotropic temperature factors taken from the isomorphous compound Ca_5Sb_3 (Martinez-Ripoll & Brauer, 1974) were refined by the least-squares procedure using the program *CRYLSQ* written by F.A. Kundell and assuming unit weights. Scattering factors used were those for neutral atoms (Hanson, Herman, Lea & Skillman, 1964) corrected for anomalous dispersion with $\Delta f' = 0.2$ and $\Delta f'' = 0.4$ for Ca, and with $\Delta f' = -4.7$ and $\Delta f'' = 11.7$ for Bi, as listed in *International Tables for X-ray Crystallography* (1962). The final residual $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.065$ is based on the parameters given in Table 1. A table listing the observed and calculated structure factors is available.* The programs used in this determination were those of the X-RAY 70 System (Stewart, Kundell & Baldwin, 1970) running on the 1108 UNIVAC computer of the University of Freiburg, Germany.

Table 1. *Positional and thermal parameters*

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i>
Ca(1)	0.0756 (5)	0.0445 (5)	0.6913 (6)	1.9 (1) Å ²
Ca(2)	0.2277 (6)	$\frac{1}{2}$	0.3208 (8)	1.9 (1)
Ca(3)	0.2912 (7)	$\frac{1}{2}$	0.8503 (8)	2.0 (1)
Ca(4)	0.5065 (6)	$\frac{1}{2}$	0.4637 (8)	1.7 (1)
Bi(1)	0.1708 (1)	-0.0136 (1)	0.0657 (1)	1.56 (2)
Bi(2)	-0.0164 (1)	$\frac{1}{2}$	0.4208 (1)	1.54 (2)

Standard deviations are given in parentheses.

Discussion

Thermal and microscopic work on the binary system Ca–Bi undertaken by Kurzyniec (1931) indicated the existence of two compounds in the system: Ca_3Bi_2 and CaBi_3 . According to Iandelli (1949), the compound CaBi_3 is not cubic. Later investigations of Brauer & Müller (1961) indicated that the stoichiometry of Ca_3Bi_2 mentioned above should be revised to Ca_7Bi_4 . As part of a programme of investigation of intermetallic compounds, we have solved the crystal structure of the latter compound. Its correct formula Ca_5Bi_3 , was deduced from this determination.

Ca_5Bi_3 is isomorphous with Ca_5Sb_3 (Martinez-Ripoll & Brauer, 1974). Its crystal structure can be described in terms of atomic layers perpendicular to the **b** direction (see Martinez-Ripoll & Brauer, 1974, Fig. 2). The number of neighbours around the calcium atoms (Table 2) can be found to be between 12 and 13 by applying a criterion similar to that proposed by Brunner & Schwarzenbach (1971). If the distances from the considered atom to all other atoms are ordered in a series according to increasing value, there is a gap or minimum

in this series which limits the area of neighbours. There are two kinds of Bi atoms. Bi(1) is surrounded by 9 calcium atoms forming the unit BiCa_9 , similar to the SbCa_9 units in the isomorphous compound Ca_5Sb_3 (Martinez-Ripoll & Brauer, 1974, Fig. 7). The Bi(2) atoms are surrounded by only 8 calcium atoms in the form shown in Fig. 8 of Martinez-Ripoll & Brauer (1974). The average values of the Bi(1)–Ca and Bi(2)–Ca distances are 3.423 and 3.263 Å, respectively. A list of all interatomic distances is given in Table 2.

Table 2. *Interatomic distances*

Estimated standard deviation ± 0.008 Å.			
Around Ca(1)		Around Ca(2)	
Ca(1)–Bi(2)	3.093 Å ($\times 1$)	Ca(2)–Bi(2)	3.218 Å ($\times 1$)
–Bi(2)	3.244 ($\times 1$)	–Bi(1)	3.340 ($\times 2$)
–Bi(1)	3.409 ($\times 1$)	–Bi(1)	3.412 ($\times 2$)
–Bi(1)	3.427 ($\times 1$)	–Bi(2)	3.840 ($\times 1$)
–Bi(1)	3.757 ($\times 1$)	–Ca(4)	3.697 ($\times 1$)
–Ca(4)	3.631 ($\times 1$)	–Ca(4)	3.746 ($\times 1$)
–Ca(3)	3.641 ($\times 1$)	–Ca(1)	3.944 ($\times 2$)
–Ca(4)	3.804 ($\times 1$)	–Ca(3)	4.049 ($\times 1$)
–Ca(1)	3.854 ($\times 1$)	–Ca(1)	4.177 ($\times 2$)
–Ca(2)	3.944 ($\times 1$)		
–Ca(1)	3.972 ($\times 1$)		
–Ca(3)	4.143 ($\times 1$)		
–Ca(2)	4.177 ($\times 1$)		
Around Ca(3)		Around Ca(4)	
Ca(3)–Bi(2)	3.118 Å ($\times 1$)	Ca(4)–Bi(2)	3.255 Å ($\times 1$)
–Bi(1)	3.349 ($\times 2$)	–Bi(1)	3.304 ($\times 2$)
–Bi(1)	3.484 ($\times 2$)	–Bi(1)	3.324 ($\times 2$)
–Ca(1)	3.641 ($\times 2$)	–Ca(1)	3.631 ($\times 2$)
–Ca(4)	3.947 ($\times 1$)	–Ca(2)	3.697 ($\times 1$)
–Ca(2)	4.049 ($\times 1$)	–Ca(2)	3.746 ($\times 1$)
–Ca(1)	4.143 ($\times 2$)	–Ca(1)	3.804 ($\times 2$)
–Ca(4)	4.258 ($\times 1$)	–Ca(3)	3.947 ($\times 1$)
		–Ca(3)	4.258 ($\times 1$)
Around Bi(1)		Around Bi(2)	
Bi(1)–Ca(4)	3.304 Å ($\times 1$)	Bi(2)–Ca(1)	3.093 Å ($\times 2$)
–Ca(4)	3.324 ($\times 1$)	–Ca(3)	3.118 ($\times 1$)
–Ca(2)	3.340 ($\times 1$)	–Ca(2)	3.218 ($\times 1$)
–Ca(3)	3.349 ($\times 1$)	–Ca(1)	3.244 ($\times 2$)
–Ca(1)	3.409 ($\times 1$)	–Ca(4)	3.255 ($\times 1$)
–Ca(2)	3.412 ($\times 1$)	–Ca(2)	3.840 ($\times 1$)
–Ca(1)	3.427 ($\times 1$)		
–Ca(3)	3.484 ($\times 1$)		
–Ca(1)	3.757 ($\times 1$)		
–Bi(1)	4.492 ($\times 1$)		
–Bi(1)	4.571 ($\times 1$)		
Averages			
Ca(1)–Bi	3.386 Å	Ca(2)–Bi	3.427 Å
–Ca	3.896	–Ca	3.962
Ca(3)–Bi	3.357	Ca(4)–Bi	3.302
–Ca	3.975	–Ca	3.815
Bi(1)–Ca	3.423	Bi(2)–Ca	3.263

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* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30445 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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The Crystal Structure of $\alpha\text{-Mg}_3\text{Sb}_2$

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$\alpha\text{-Mg}_3\text{Sb}_2$ crystallizes as an La_2O_3 -type structure, space group $P\bar{3}m1$, with one formula unit in a cell of dimensions $a = 4.568 \pm 0.003$ and $c = 7.229 \pm 0.004$ Å. The calculated density is 4.02 g cm^{-3} . This crystal structure has been solved by three-dimensional Patterson synthesis and refined by the least-squares procedure, including 387 reciprocal points, to a residual of $R = 0.069$. No 'micro-twinning' occurs as described for La_2O_3 .

Introduction

Early work on the binary system Mg–Sb undertaken by Grube (1906) showed the existence of a phase of composition Mg_3Sb_2 with a melting point of 1245°C (Bolshakov, Bulonkov & Tsirlin, 1962). This compound ($\alpha\text{-Mg}_3\text{Sb}_2$) was identified by Zintl & Husemann (1933) as being isotypic with La_2O_3 . The existence of a polymorphic transformation from $\alpha\text{-Mg}_3\text{Sb}_2$ to a cubic Mn_2O_3 -type structure (presumably $\beta\text{-Mg}_3\text{Sb}_2$) was suggested by Zintl (1934).

More recently a statistical distribution in the crystal structure of La_2O_3 has been reported (Müller-Buschbaum & von Schnering, 1965) which is inconsistent with the original model (Pauling, 1929). In order to elucidate whether $\alpha\text{-Mg}_3\text{Sb}_2$ presents the same kind of 'micro-twinning' described for La_2O_3 , and as a part of a programme aimed at achieving a better understanding of the structural principles of intermetallic compounds with extremely positive metals we have solved the crystal structure of $\alpha\text{-Mg}_3\text{Sb}_2$ using single-crystal diffraction data.

Experimental

Single crystals of $\alpha\text{-Mg}_3\text{Sb}_2$ were prepared by cooling a melt of composition $3\text{Mg} + 2\text{Sb}$ with a small excess of magnesium from 1100°C to room temperature in argon atmosphere. They have a metallic appearance and are resistant to air.

Precession photographs taken with Mo $K\alpha$ radiation showed hexagonal symmetry. The systematic absences

correspond to the space groups $P3m1$, $P31m$, $P312$, $P321$, $P\bar{3}1m$ and $P\bar{3}m1$. As discussed later, the space group $P\bar{3}m1$ was assumed. A least-squares fit of the θ values for several reflexions led to the following dimensions: $a = 4.568 \pm 0.003$ and $c = 7.229 \pm 0.004$ Å, in good agreement with the values 4.573 and 7.229 Å reported previously by Zintl & Husemann (1933). The calculated density with one formula unit in the cell is 4.02 g cm^{-3} , agreeing well with the macroscopic value of 4.09 g cm^{-3} (Weibke, 1930).

The intensity data from seven reciprocal layers perpendicular to the a axis were obtained from a plate-like single crystal ($0.08 \times 0.24 \times 0.32$ mm) mounted on a single-crystal Huber diffractometer (RHD 402) on-line to a PDP-8 computer. Graphite-monochromated Mo $K\alpha$ radiation was used in conjunction with a scintillation detector and pulse-height discrimination. 405 independent reflexions were collected in the range $3^\circ < \theta < 50^\circ$. Of this total, 387 reflexions were considered 'observed' according to the criterion $I > 2\sigma(I)$ and used in the refinement. The intensities were corrected for Lorentz and polarization effects in the usual manner. Absorption corrections ($\mu R \approx 1.7$) were considered irrelevant for the purpose of this study. In any case, such corrections would be tedious because of the irregular form of the crystal.

Determination of the structure

The first step in the solution of this crystal structure was based on the interpretation of the three-dimensional Patterson function. The peak distribution in the