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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

Patterson synthesis eliminated the space groups $P31m$, $P312$ and $P\bar{3}1m$. All maxima could be explained in terms of the same arrangement of atoms in the space groups $P3m1$, $P321$ and $P\bar{3}m1$. As the atomic arrangement was found to be centrosymmetric, the space group $P\bar{3}m1$ was assumed.

Structure factors based on the Patterson coordinates, assuming an initial overall isotropic temperature factor of 1.18 \AA^2 obtained from the Wilson plot, correspond to $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.12$. Scattering factors used were those for neutral atoms (Hanson, Herman, Lea & Skillman, 1964). The anomalous dispersion corrections listed in *International Tables for X-ray Crystallography* (1962) were also used.

Table 1. *Positional and thermal parameters*

Standard deviations are given in parentheses.

	x/a	y/b	z/c	B
Mg(1)	0	0	0	2.1 (2) \AA^2
Mg(2)	$\frac{1}{3}$	$\frac{2}{3}$	0.6339 (9)	1.4 (1)
Sb	$\frac{1}{3}$	$\frac{2}{3}$	0.2283 (1)	1.05 (2)

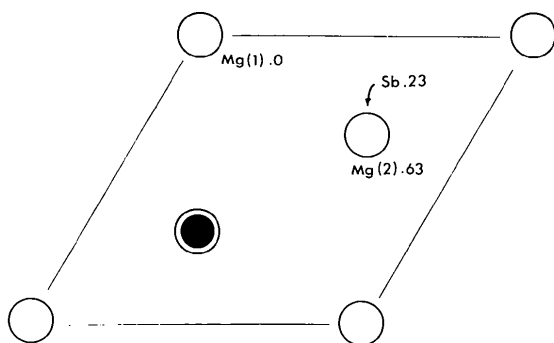


Fig. 1. The structure of $\alpha\text{-Mg}_3\text{Sb}_2$ projected on the (001) plane. The heights of the atoms are given as fractions of the c parameter.

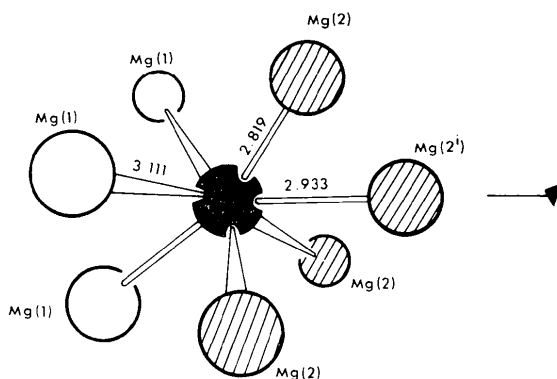


Fig. 2. Arrangement of magnesium atoms around Sb. The bond lengths are given in \AA .

Refinement was carried out by the full-matrix least-squares procedure using the program *CRYLSQ* written by F.A. Kundell and assuming unit weights. The final conventional R index is 0.069 based on the parameters given in Table 1. A table listing the observed and calculated structure factors is available.*

Description and discussion of the structure

$\alpha\text{-Mg}_3\text{Sb}_2$ crystallizes in the La_2O_3 -type structure. Although the La_2O_3 structure has been recently discussed (Müller-Buschbaum & von Schnering, 1965), the structure type of $\alpha\text{-Mg}_3\text{Sb}_2$ corresponds exactly to that described originally by Pauling (1929).

Fig. 1 shows a view of the structure projected on the (001) plane. The magnesium atoms occupy two different crystallographic sites corresponding to the point symmetries $\bar{3}m$, Mg(1), and $3m$, Mg(2). There is one crystallographically independent Sb atom only, which corresponds to the point symmetry $3m$. The crystal structure of $\alpha\text{-Mg}_3\text{Sb}_2$ can be described in terms of SbMg_7 units (Fig. 2). Each of these units contains three Mg(1) and four Mg(2) atoms. Six of the magnesium atoms are arranged at the corners of a trigonal antiprism whose centre is occupied by the antimony atom. The seventh Mg atom approximates the Sb atom in the direction of the threefold axis of the group (Fig. 2). Each Mg(1) atom is surrounded by 12 neighbours [$6\text{Sb} + 6\text{Mg}(2)$] and each Mg(2) atom has ten neighbours [$1\text{Sb} + 3\text{Sb} + 3\text{Mg}(2) + 3\text{Mg}(1)$]. A list of all interatomic distances is given in Table 2.

Table 2. *Interatomic distances*

Estimated standard deviation $\pm 0.005 \text{ \AA}$.

Around Mg(1)		Around Mg(2)	
Mg(1)–Sb	3.111 \AA ($\times 6$)	Mg(2)–Sb	2.819 \AA ($\times 3$)
Mg(1)–Mg(2)	3.736 ($\times 6$)	Mg(2)–Sb	2.933 ($\times 1$)
		Mg(2)–Mg(2)	3.272 ($\times 3$)
		Mg(2)–Mg(1)	3.736 ($\times 3$)
Around Sb			
Sb–Mg(2)	2.819 \AA ($\times 3$)		
Sb–Mg(2)	2.933 ($\times 1$)		
Sb–Mg(1)	3.111 ($\times 3$)		
Average	2.961		

The Sb–Mg distances in the group SbMg_7 are not all equal (Fig. 2). The three Mg(1) atoms are at 3.111 \AA , agreeing very well with the value of 3.12 \AA predicted from the sum of metallic radii given by Pauling (1947) and assuming coordination numbers of 7 and 12 for Sb and Mg(1), respectively. The Sb–Mg(2) distances of 2.819 and 2.933 \AA are shorter ($\sim 7\%$) than the pre-

* This table has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30446 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

dicted value of 3.09 Å assuming coordination number 10 for the Mg(2) atoms. The mean value of all the Sb–Mg distances is 2.961 Å, ~4% shorter than the predicted value (3.10 Å). No short Mg–Mg distances are present in this structure, in contrast to the short Ca–Ca, Sr–Sr and Ba–Ba distances appearing in the structures of Ca₅Sb₃, Ca₅Bi₃, Sr₅Sb₃, Sr₂Sb and Ba₂Bi (see Fig. 3 for references). The minimum Mg–Mg distance of 3.272 Å compares with the predicted value of 3.15 Å obtained from the sum of metallic radii.

It seems to be a common feature of the Ca, Sr and Ba compounds with the main group V elements (independently of composition or structure) to present an appreciable 'volumen contraction' when the volumes per formula unit of the compounds are compared with the volumes of the component metals computed in the right stoichiometry (Fig. 3). This 'volumen contraction' is negligible, however, in the case of the Mg compounds. One may interpret this situation as being due to a more extensive transfer of electrons from the heavy alkaline earth metal atoms to the group V element atoms than is the case with the Mg atoms, in spite of the fact that the Mg compounds have salt-like formulae whereas the Ca, Sr and Ba compounds do not.

The numerical calculations in the analysis were performed using the X-RAY 70 System of crystallographic programs (Stewart, Kundell & Baldwin, 1970) on the 1108 UNIVAC computer of the University of Freiburg, Germany. We acknowledge the facilities given by Huber Diffraktions-Technik to obtain the intensity data. We are indebted to the Deutsche Forschungsgemeinschaft for financial support given to M.M.R.

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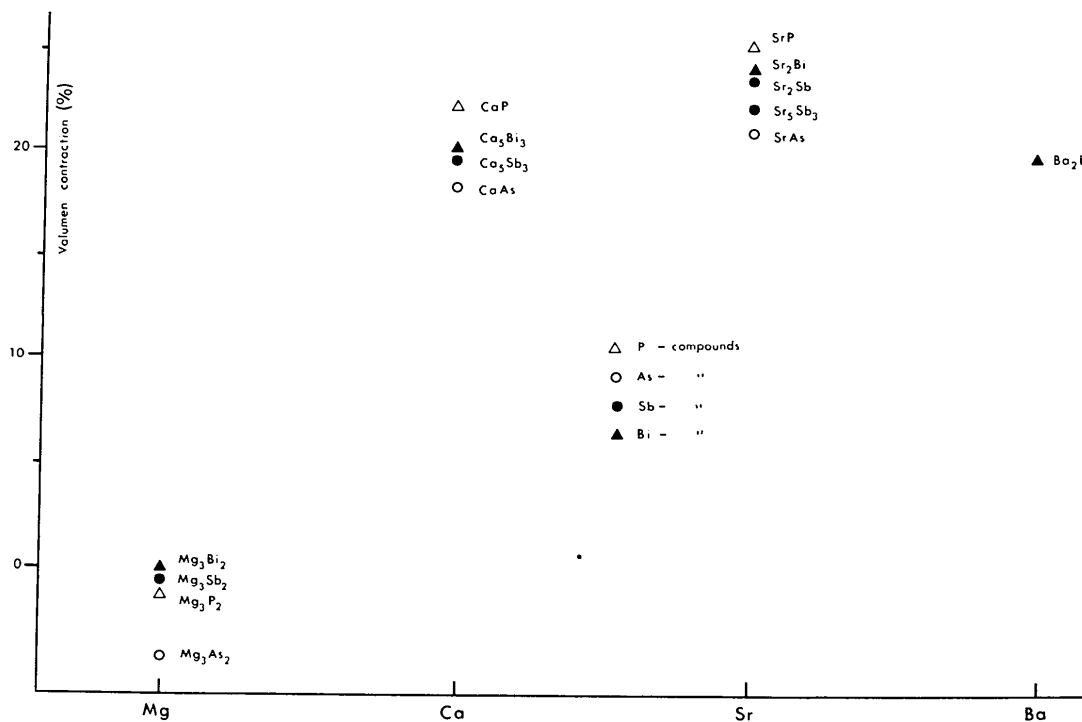


Fig. 3. 'Volumen contraction' of the Mg, Ca, Sr and Ba compounds with the elements of the main group V. References: Mg₃Sb₂, present paper; Mg₃Bi₂, Mg₃P₂, Mg₃As₂, Zintl & Husemann (1933); CaP, CaAs, SrP, SrAs, Iandelli & Franceschi (1973); Ca₅Sb₃, Martinez-Ripoll & Brauer (1974); Ca₅Bi₃, Martinez-Ripoll, Haase & Brauer (1974a); Sr₅Sb₃, Martinez-Ripoll & Brauer (1973); Sr₂Sb, Martinez-Ripoll, Haase & Brauer (1973); Sr₂Bi, Brauer & Müller (1961); Ba₂Bi, Martinez-Ripoll, Haase & Brauer (1974b).

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Structure Cristalline et Moléculaire de l'Indazole

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(Reçu le 26 novembre 1973, accepté le 17 décembre 1973)

Indazole, $C_7N_2H_6$, crystallizes in space group $P2_1$ in a unit cell of dimensions $a=7.57$, $b=5.76$, $c=7.70$ Å, $\beta=119.47^\circ$, $Z=2$. 580 independent intensities were collected on an automatic diffractometer by a θ - 2θ scan method with Cu $K\alpha$ radiation. The structure was refined by full-matrix least-squares calculations to a conventional R of 0.075.

Nous avons entrepris sur la proposition de M Elguero du Laboratoire de M le Professeur Jacquier l'étude d'un groupe de trois produits comprenant le benzotriazole, le benzimidazole et l'indazole. Pour l'indazole, le problème à résoudre était de savoir à quel atome d'azote est lié l'hydrogène de l'hétérocycle.

Partie expérimentale

Le cristal était de forme parallélépipédique de dimensions $0,1 \times 0,1 \times 0,3$ mm allongée suivant l'axe b . Après les études préliminaires faites sur chambre de Weissenberg, nous avons fait une première détermination approximative des paramètres. Ensuite, l'utilisation d'un diffractomètre Enraf-Nonius nous a permis d'observer la loi d'extinction suivant $0k0$ (extinction pour $k=2n+1$), et de mesurer avec précision les angles de diffraction d'un grand nombre de réflexions à partir desquelles un affinement nous a donné une valeur plus précise des paramètres.

Nous avons obtenu pour la densité mesurée par la méthode de flottaison dans une solution d'IK une valeur de 1,32. Ceci imposait deux molécules par maille et une densité calculée indentique de 1,32. Deux groupes de symétrie étaient possibles, $P2_1$ (2 positions équivalentes par maille) ou $P2_1/m$ (4 positions équivalentes); pour ce dernier groupe il fallait donc que la molécule soit parfaitement plane et se trouve dans le plan de symétrie, l'examen de la fonction de Patterson nous a fait éliminer cette hypothèse.

Nous avons mesuré 557 réflexions non nulles sur diffractomètre automatique Enraf-Nonius à la température ambiante. Le rayonnement $K\alpha$ du cuivre a été

utilisé après réflexion sur un monochromateur de graphite.

Vu les faibles valeurs du coefficient d'absorption linéaire ($6,40 \text{ cm}^{-1}$) et des dimensions du cristal, nous avons pu négliger la correction d'absorption; seule a été effectuée la correction Lorentz-polarisation.

Les facteurs de diffusion atomique sont ceux de Doyle & Turner (1968) pour les atomes de carbone et d'azote et ceux de Stewart, Davidson & Simpson (1965) pour les atomes d'hydrogène.

Données cristallographiques

Formule: $C_7N_2H_6$
 Poids moléculaire 118,12
 Groupe de symétrie $P2_1$
 $a=7,57 \pm 0,006$ Å
 $b=5,76 \pm 0,005$
 $c=7,70 \pm 0,006$
 $\beta=119,5 \pm 0,1^\circ$
 $V=291$ Å³
 $Z=2$
 $d_{\text{obs}}=1,32 \text{ g cm}^{-3}$
 $d_{\text{cal}}=1,32$
 $\mu(\text{Cu } K\alpha)=6,40 \text{ cm}^{-1}$

Détermination de la structure

Nous avons d'abord déterminé le facteur d'agitation thermique global $B=2,59$ et le facteur de mise à l'échelle absolue $K=0,40$ par la méthode de Wilson (1942). A partir de ces valeurs, nous avons calculé les facteurs de structure normalisés E . La structure a été déterminée par les méthodes directes en utilisant le