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# The Crystal Structure of $Y_5Bi_3$ and its Relation to the $Mn_5Si_3$ and the $Yb_5Sb_3$ Type Structures

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$Y_5Bi_3$ is orthorhombic, *Pnma*, $a=8{\cdot}179$ (1), $b=9{\cdot}401$ (1), $c=11{\cdot}957$ (1) Å, $Z=4$. The structure was refined to an $R$ value of 3·1% for 1427 diffractometer data corrected for absorption and with anomalous dispersion effects included. The structure is composed of $[BiY_6]$ trigonal prisms stacked in columns which share edges to form hexagonal channels containing ribbons of $[Bi_2Y_2]$ parallelograms sharing corners; the coordination distances for Bi–Y range from 3·05 to 3·47 with a mean of 3·24 Å; for Y–Y from 3·36 to 4·39 with a mean of 3·81 Å and for Bi–Bi from 4·15 to 4·48 with a mean of 4·34 Å.

## Introduction

In a recent survey of the binary Ln–Bi system (Ln= rare earth element or Y) two structures with a nominal 5:3 composition were found (Yoshihara, Taylor, Calvert & Despault, 1975). The elements La, Ce, Pr and Nd form the $Mn_5Si_3$ type and Y, Dy, Ho, Er and Tm form the $Y_5Bi_3$ type (Schmidt, McMasters & Lichtenberg, 1969) whereas Gd and Tb form both structures. The present study was undertaken to clarify the structural and compositional relationship between the two types; $Y_5Bi_3$ was the only phase from which suitable crystals were obtained.

## Experimental

Intensity data were collected, using Mo $K\alpha$ radiation monochromatized by the 0002 reflexion of graphite, from a small crystal ($\simeq 70\times30\times30$ $\mu$m) mounted on a rod and sealed into an $SiO_2$ tube under an inert atmosphere. This crystal was prepared from the melt by slow cooling from 1600 °C in a sealed Ta tube. The Picker diffractometer was controlled by a PDP-8e computer with a local Fortran IV program (Grant & Gabe, 1974). Four symmetry-related sets of reflexions were measured by the $\theta$–$2\theta$ scan technique up to $2\theta=60°$; background measurements were taken for half the total scan time at each end of the scan range, which was varied as $(0{\cdot}5+0{\cdot}7\tan\theta+0{\cdot}7)°$; thirty-six reflexions were centred individually and the angles derived were used to refine the lattice parameters by a least-squares process. The four sets of intensities were averaged after the application of Lorentz, polarization and absorption corrections to give a total of 1427 independent reflexions. The absorption corrections were evaluated by Gaussian integration with 10 grid points along each orthogonal direction (Gabe & O'Byrne, 1970). The crystal shape was measured using a special high-resolution microscope mounted on the chi-circle. Intensity scans after rotation ($\psi$) about the diffraction vector were carried out for a number of reflexions. The observed curves of intensity against $\psi$ and of the calculated absorption ($A^*$) against $\psi$ were similar in amplitude and shape, but with a $\psi$ difference of between 5 and 20° which either led or lagged according to the side of the chi-circle ($\psi\simeq90$ or 270°). The calculated absorption correction was therefore applied with the appropriate $\psi$ shift. The internal consistency among four symmetry-related intensities was 9·5% after the absorption correction and 14·5% before. The values of the transmission coefficient ranged from 0·019 to 0·095. Subsequent work (Wang, Gabe & Calvert, 1976) showed that this $\psi$ shift was probably due to a misaligned diffracted beam tunnel but by that time the original $Y_5Bi_3$ crystal had decomposed and no other could be found so that the data already collected were used to determine the structure.

*Crystallographic data*

$Y_5Bi_3$, $M=1071{\cdot}5$
Space group *Pnma*, $Z=4$
$a=8{\cdot}179$ (1), $b=9{\cdot}401$ (1), $c=11{\cdot}957$ (1) Å
$U=919{\cdot}3$ Å$^3$, $D_x=7{\cdot}52$ g cm$^{-3}$
$\mu_l$(Mo $K\alpha$) = 837 cm$^{-1}$, $F(000)=1776$.

## Structure refinement

The Bi atom coordinates were found from a Patterson map and the Y atom coordinates were derived from a Fourier difference map based on the Bi atom contributions. The parameters were refined by a Gauss–Seidel block-diagonal least-squares analysis (Syntex, 1974). The scattering factors were calculated with the analytical approximation $f_s=\sum a_i\exp(-b_iS^2)\ldots$ and allowance for anomalous dispersion using constants from *International Tables for X-ray Crystallography* (1974). All calculations were carried out on the PDP-8e computer in the laboratory using local programs and programs adapted from elsewhere (Syntex, 1974). The final agreement indices are $R_2=[\sum\omega(F_o-F_c)^2/\sum\omega F_o^2]^{1/2}=3{\cdot}1\%$ and $R=(\sum|F_o-F_c|/\sum F_o)=4{\cdot}2\%$ where $\omega=1/\sigma^2$ and $\sigma$ is the weight based on counting statistics; the goodness of fit $[\sum\omega(F_o-F_c)^2/\mathrm{NO}-\mathrm{NV}]^{1/2}$ where NO = 1022 and NV = 63 is 0·85; reflexions are considered observed if $F_o>2\sigma$. The final parameters are given in Table 1 and coordination distances (Frank & Kasper,

1958) in Table 2. The final difference map based on these parameters showed no significant detail at atomic sites or elsewhere and therefore it appears that the occupancy of all sites is unity and that there are no interstitial atoms. The structure factor tables are available.* The lattice parameters derived from the powder pattern, $a=8{\cdot}1895$ (4), $b=9{\cdot}4202$ (4), $c=11{\cdot}9753$ (6) Å, differ significantly from those observed for the crystal studied (see above); similar differences have been reported for other cases (Hubbard, Swanson & Mauer, 1975) and have been observed in this laboratory for some, but not all, binary compounds (Table 3).

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31467 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

### Description of the structure

$Y_5Bi_3$ has a double layer structure (Fig. 1). Layers of Y atoms in the special positions 4(*c*) with $y=\frac{1}{4}$ and $\frac{3}{4}$, almost superimposed, form triangle–hexagon networks (Fig. 2) with Bi atoms also at $y=\frac{1}{4}$ and $\frac{3}{4}$ almost centring the hexagons but displaced towards opposite ends on alternate layers. These successive layers of Y atoms thus form slightly skew hexagonal and trigonal prisms. The Bi and Y atoms, in the general positions 8(*d*) with $y\simeq 0$ or $\frac{1}{2}$ form a puckered diamond–pentagon network; the Bi atoms centre the trigonal prisms while pairs of Y atoms centre the hexagonal prisms.

Thus the $Y_5Bi_3$ structure is composed of columns of $[BiY_6]$ trigonal prisms stacked parallel to **b** on their triangular faces and sharing edges to form hexagonal channels of Y atoms (7·5 × 5 Å, Fig. 1) occupied by $[Y_2Bi_2]$ parallelograms sharing Bi corners to form a slightly twisted ribbon. This is similar to the $Rh_5Ge_3$

Table 1. *Fractional positional coordinates and thermal ellipsoids* (Å² × 10²)

Temperature factor = exp $[-\frac{1}{4}(h^2a^{*2}B_{11}+k^2b^{*2}B_{22}+l^2c^{*2}B_{33}+hka^*b^*B_{12}+hla^*c^*B_{13}+klb^*c^*B_{23})]$.

| | Site | *x* | *y* | *z* | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Bi(1) | 8(*d*) | 0·0664 (1) | −0·0030 (1) | 0·1740 (1) | 96 (2) | 74 (2) | 70 (2) | 6 (3) | −13 (2) | −2 (2) |
| Bi(2) | 4(*c*) | 0·0889 (1) | 0·25 | 0·4577 (1) | 85 (3) | 81 (3) | 71 (3) | 0 | 1 (3) | 0 |
| Y(1) | 4(*c*) | 0·4726 (3) | 0·25 | 0·4902 (2) | 63 (10) | 99 (7) | 83 (7) | 0 | −5 (8) | 0 |
| Y(2) | 4(*c*) | 0·3146 (4) | 0·25 | 0·2194 (2) | 78 (10) | 95 (5) | 84 (8) | 0 | 14 (8) | 0 |
| Y(3) | 8(*d*) | 0·1934 (3) | 0·5607 (2) | 0·4404 (1) | 90 (6) | 81 (6) | 75 (5) | −8 (6) | 7 (6) | −7 (4) |
| Y(4) | 4(*c*) | 0·1458 (4) | 0·25 | 0·7126 (2) | 113 (10) | 115 (9) | 65 (7) | 0 | 8 (8) | 0 |

Table 2. *Coordination distances* (Å); *e.s.d.'s from* 0·003 *to* 0·004 Å

| Bi(1) | | Bi(2) | | Y(3) | |
|---|---|---|---|---|---|
| Y(2) | 3·174 | (×2) Y(3) | 3·051 | Bi(2) | 3·051 |
| Y(1) | 3·178 | Y(2) | 3·085 | Bi(2) | 3·159 |
| Y(4) | 3·200 | Y(4) | 3·083 | Bi(1) | 3·387 |
| Y(1) | 3·213 | (×2) Y(3) | 3·159 | Bi(1) | 3·395 |
| Y(4) | 3·339 | Y(1) | 3·162 | Bi(1) | 3·466 |
| Y(3) | 3·387 | Y(2) | 3·395 | Y(1) | 3·363 |
| Y(3) | 3·395 | (×2) Bi(1) | 4·147 | Y(4) | 3·509 |
| Y(2) | 3·395 | (×2) Bi(1) | 4·475 | Y(3) | 3·559 |
| Y(3) | 3·466 | | | Y(3) | 3·653 |
| Bi(2) | 4·147 | | | Y(1) | 3·755 |
| Bi(1) | 4·300 | | | Y(4) | 3·770 |
| Bi(2) | 4·475 | | | Y(2) | 3·781 |
| (×2) Bi(1) | 4·475 | | | Y(2) | 4·062 |
| | | | | Y(4) | 4·390 |
| CN | 14 | | 12 | | 14 |
| Mean Bi–Y | 3·31 (11) | | 3·14 (11) | | 3·29 (18) |
| Mean Y–Y | — | | — | | 3·76 (31) |
| Mean Bi–Bi | 4·37 (15) | | 4·31 (19) | | — |

| Y(1) | | Y(2) | | Y(4) | |
|---|---|---|---|---|---|
| Bi(2) | 3·162 | Bi(2) | 3·085 | Bi(2) | 3·083 |
| (×2) Bi(1) | 3·178 | (×2) Bi(1) | 3·174 | (×2) Bi(1) | 3·200 |
| (×2) Bi(1) | 3·213 | (×2) Bi(1) | 3·395 | (×2) Bi(1) | 3·339 |
| (×2) Y(3) | 3·363 | Bi(2) | 3·395 | (×2) Y(3) | 3·509 |
| Y(2) | 3·487 | Y(1) | 3·487 | Y(1) | 3·770 |
| (×2) Y(3) | 3·755 | Y(1) | 3·756 | (×2) Y(3) | 3·770 |
| Y(2) | 3·756 | (×2) Y(3) | 3·781 | Y(1) | 3·825 |
| Y(4) | 3·770 | (×2) Y(3) | 4·062 | (×2) Y(4) | 4·186 |
| Y(4) | 3·825 | (×2) Y(2) | 4·154 | (×2) Y(3) | 4·390 |
| CN | 13 | | 14 | | 15 |
| Mean Y–Bi | 3·19 (2) | | 3·27 (14) | | 3·23 (15) |
| Mean Y–Y | 3·64 (20) | | 3·91 (24) | | 3·93 (33) |

Overall mean values Y–Bi = 3·24, Y–Y = 3·81, Bi–Bi = 4·34.

Table 3. *Observed and calculated powder pattern for* $Y_5Bi_3$

Cu $K\alpha_1$ radiation ($\lambda = 1{\cdot}54051$ Å), 80 mm Guinier camera, 25 °C, Si internal standard ($a = 5{\cdot}43052$ Å). The refined parameters derived from the powder pattern, $a = 8{\cdot}1895$ (4), $b = 9{\cdot}4202$ (4), $c = 11{\cdot}9753$ (6) Å ($M_{20} = 29$) were used to calculate the $d$ values; the intensities were calculated from the parameters of Table 1. The specimen was prepared by crushing an ingot of composition $Y_{2.5}Bi$ which had been slowly cooled from a temperature just above the liquidus. The observed intensities are reported as VW (very weak), W (weak), M (medium), S (strong), VS (very strong).

| $D_{obs}$ | $D_{calc}$ | $h\ k\ l$ | $I_{obs}$ | $I_{calc}$ |
|---|---|---|---|---|
| 7·42 | 7·40 | 0 1 1 | VW | 1·70 |
| 6·80 | 6·76 | 1 0 1 | VW | 0·50 |
| 5·49 | 5·49 | 1 1 1 | M | 8·85 |
| 4·302 | 4·300 | 1 1 2 | W | 3·83 |
| 4·094 | 4·095 | 2 0 0 | M | 14·58 |
| | 3·875 | 2 0 1 | | 21·92 |
| 3·865 | 3·865 | 1 2 1 | S | 51·81 |
| 3·756 | 3·755 | 2 1 0 | W | 7·32 |
| 3·702 | 3·702 | 0 2 2 | M | 25·89 |
| 3·676 | 3·675 | 0 1 3 | W | 4·12 |
| 3·590 | 3·588 | 1 0 3 | S | 60·15 |
| 3·371 | 3·373 | 1 2 2 | VW | 1·20 |
| 3·353 | 3·353 | 1 1 3 | VW | 2·58 |
| 3·182 | 3·181 | 2 1 2 | W | 4·02 |
| 3·037 | 3·037 | 0 3 1 | W | 5·93 |
| 2·993 | 2·994 | 0 0 4 | VS | 5·07 |
| | 2·992 | 2 2 1 | | 91·50 |
| | 2·858 | 2 0 3 | | 25·14 |
| 2·854 | 2·854 | 1 2 3 | VS | 83·94 |
| 2·846 | 2·848 | 1 3 1 | M | 33·98 |
| 2·812 | 2·812 | 1 0 4 | S | 70·20 |
| 2·746 | 2·746 | 2 2 2 | S | 100·00 |
| 2·734 | 2·735 | 2 1 3 | W | 11·57 |
| 2·696 | 2·694 | 1 1 4 | W | 5·79 |
| 2·661 | 2·662 | 3 0 1 | M | 24·29 |
| 2·633 | 2·633 | 1 3 2 | VW | 2·97 |
| 2·561 | 2·561 | 3 1 1 | M | 30·14 |
| 2·527 | 2·527 | 0 2 4 | M | 32·91 |
| 2·491 | 2·492 | 2 3 0 | W | 14·91 |
| 2·485 | 2·484 | 3 0 2 | W | 12·03 |
| 2·468 | 2·468 | 0 3 3 | W | 15·00 |
| 2·443 | 2·444 | 2 2 3 | W | 13·98 |
| | 2·440 | 2 3 1 | | 0·59 |
| 2·414 | 2·417 | 2 0 4 | VW | 0·15 |
| | 2·414 | 1 2 4 | | 1·25 |
| 2·398 | 2·402 | 3 1 2 | VW | 0·25 |
| 2·354 | 2·355 | 0 4 0 | S | 56·16 |
| 2·339 | 2·341 | 2 1 4 | W | 1·04 |
| 2·321 | 2·321 | 0 1 5 | W | 4·49 |
| | 2·317 | 3 2 1 | | 0·22 |
| 2·299 | 2·301 | 2 3 2 | M | 8·51 |
| | 2·299 | 1 0 5 | | 7·44 |
| 2·233 | 2·233 | 1 1 5 | VW | 0·89 |
| 2·222 | 2·224 | 1 4 1 | VW | 1·25 |
| 2·197 | 2·197 | 3 2 2 | S | 48·68 |
| | 2·192 | 0 4 2 | | 1·88 |
| 2·150 | 2·150 | 2 2 4 | W | 5·85 |
| 2·117 | 2·117 | 1 4 2 | W | 3·86 |
| 2·095 | 2·095 | 1 3 4 | W | 10·23 |
| 2·066 | 2·066 | 1 2 5 | M | 17·65 |
| 2·042 | 2·047 | 4 0 0 | W | 1·01 |
| | 2·041 | 2 4 0 | | 11·40 |
| 2·030 | 2·033 | 3 2 3 | W | 0·83 |
| | 2·030 | 3 3 1 | | 5·14 |
| 2·018 | 2·019 | 2 1 5 | S | 3·45 |
| | 2·018 | 4 0 1 | | 18·71 |
| | 2·017 | 3 0 4 | | 19·11 |
| 2·001 | 2·001 | 4 1 0 | W | 3·66 |
| 1·996 | 1·996 | 0 0 6 | W | 3·98 |

Table 3 (*cont.*)

| | | | | |
|---|---|---|---|---|
| 1·969 | 1·973 | 4 1 1 | M | 0·26 |
| | 1·969 | 1 4 3 | | 19·42 |
| 1·948 | 1·948 | 3 3 2 | VW | 2·33 |
| 1·905 | 1·904 | 0 3 5 | W | 10·82 |
| | 1·899 | 1 1 6 | | 1·49 |
| | 1·898 | 4 1 2 | | 1·12 |
| 1·893 | 1·893 | 2 2 5 | W | 7·89 |
| 1·877 | 1·878 | 4 2 0 | VW | 0·94 |
| 1·855 | 1·855 | 4 2 1 | VW | 2·51 |
| | 1·854 | 3 2 4 | | 1·48 |
| | 1·851 | 0 4 4 | | 1·96 |
| 1·839 | 1·838 | 0 2 6 | W | 5·15 |
| 1·831 | 1·831 | 3 3 3 | W | 2·20 |
| 1·824 | 1·822 | 4 0 3 | W | 3·20 |
| 1·818 | 1·818 | 2 4 3 | W | 5·52 |
| | 1·815 | 1 5 1 | | 0·08 |
| 1·806 | 1·805 | 1 4 4 | M | 17·27 |
| 1·800 | 1·800 | 3 0 5 | VW | 4·44 |
| 1·794 | 1·794 | 2 0 6 | M | 12·42 |
| | 1·793 | 1 2 6 | | 0·96 |
| 1·769 | 1·768 | 3 1 5 | W | 2·42 |
| 1·764 | 1·764 | 3 4 1 | W | 4·44 |
| 1·709 | 1·712 | 2 5 0 | W | 0·06 |
| | 1·709 | 3 4 2 | | 4·57 |
| 1·698 | 1·699 | 4 2 3 | W | 2·72 |
| | 1·698 | 4 3 1 | | 0·25 |
| | 1·697 | 3 3 4 | | 3·28 |
| 1·682 | 1·687 | 2 4 4 | W | 0·05 |
| | 1·683 | 0 1 7 | | 1·32 |
| | 1·682 | 3 2 5 | | 2·83 |
| 1·676 | 1·677 | 2 2 6 | M | 4·51 |
| | 1·675 | 1 0 7 | | 5·81 |
| 1·650 | 1·650 | 1 3 6 | VW | 2·21 |
| | 1·650 | 1 1 7 | | 0·20 |
| | 1·649 | 4 3 2 | | 0·86 |
| 1·644 | 1·646 | 2 5 2 | VW | 0·20 |
| | 1·645 | 1 4 5 | | 4·26 |
| 1·599 | 1·599 | 5 1 1 | W | 1·56 |
| 1·580 | 1·580 | 5 0 2 | M | 1·72 |
| | 1·579 | 2 0 7 | | 10·61 |
| | 1·578 | 1 2 7 | | 0·86 |
| 1·573 | 1·576 | 4 3 3 | W | 0·90 |
| | 1·573 | 2 5 3 | | 4·14 |
| | 1·570 | 0 6 0 | | 0·63 |
| 1·557 | 1·562 | 3 3 5 | W | 1·81 |
| | 1·558 | 5 1 2 | | 0·96 |
| | 1·558 | 2 3 6 | | 0·38 |
| | 1·557 | 2 1 7 | | 1·77 |
| | 1·556 | 4 0 5 | | 2·37 |
| | 1·554 | 2 4 5 | | 1·01 |
| 1·5380 | 1·5378 | 3 5 1 | W | 8·32 |
| | 1·5343 | 5 2 1 | | 13·36 |
| 1·5321 | 1·5324 | 4 4 1 | S | 18·71 |
| | 1·5320 | 3 4 4 | | 20·76 |
| 1·5243 | 1·5245 | 3 2 6 | W | 9·08 |
| 1·5187 | 1·5187 | 0 6 2 | W | 5·97 |
| 1·5029 | 1·5023 | 0 3 7 | W | 3·10 |
| 1·4977 | 1·4978 | 5 2 2 | M | 10·05 |
| 1·4780 | 1·4777 | 4 2 5 | M | 23·35 |
| 1·4658 | 1·4660 | 2 6 0 | VW | 2·17 |
| 1·4553 | 1·4551 | 2 6 1 | M | 6·43 |
| | 1·4548 | 1 1 8 | | 0·89 |
| 1·4383 | 1·4384 | 1 6 3 | M | 7·41 |
| 1·4305 | 1·4303 | 3 4 5 | VW | 5·20 |
| 1·4272 | 1·4272 | 2 4 6 | W | 7·28 |
| 1·4241 | 1·4239 | 2 6 2 | VW | 5·66 |
| 1·4208 | 1·4205 | 5 1 4 | W | 4·99 |
| 1·4059 | 1·4059 | 2 0 8 | W | 0·07 |
| | 1·4054 | 1 2 8 | | 5·71 |
| 1·3905 | 1·3905 | 2 1 8 | W | 0·54 |
| | 1·3904 | 0 6 4 | | 4·71 |

Table 3 (*cont.*)

| | | | | |
|---|---|---|---|---|
| 1·3868 | 1·3864 | 4 5 0 | VW | 1·82 |
| 1·3755 | 1·3761 | 2 6 3 | W | 5·78 |
| 1·3652 | 1·3649 | 6 0 0 | W | 0·69 |
| | 1·3648 | 1 4 7 | | 3·87 |

structure (Geller, 1955) where $[Ge_2Rh_2]$ rhombs sharing Ge corners occupy hexagonal channels.

Figs. 1 and 2 omit the coordination between the Bi atoms in the hexagons and the Y atoms comprising the hexagons. When these are included the layers at $\frac{1}{4}$ and $\frac{3}{4}$ can be described (using Schläfli symbols) (Pearson, 1972) $3^45+3^55+3^35+3^2535$ (1:1:1:1) and the layers at $\simeq 0,\frac{1}{2}$ are $45^3+45^2$ (1:1). The coordinations (Table 2) resulting from this relatively complex stacking are 12 and 14 vertex polyhedra based on trigonal prisms for the Bi atoms and irregular 13, 14 or 15 vertex polyhedra for the Y atoms. The 14-vertex polyhedron for Y(3) has geometrical features which are noteworthy. Considered in sequence along the *b* axis, this polyhedron [Fig. 3(*a*)] consists of a distorted square, a buckled square, a pentagon and finally a single atom. This vertex is itself a Y(3) atom which is the centre of a second 14 vertex polyhedron related to the first by a mirror plane containing the pentagon. The whole assemblage thus forms a 21 vertex polyhedron centred by a pair of Y(3) atoms. Alternately, considering a pair of Y(3) atoms linked by a centre [Fig. 3(*b*)] and extended along ⟨103⟩ we have a 20 vertex polyhedron comprised of a vertex atom, a boat form hexagon, a chair form hexagon, a boat hexagon and a vertex atom; however, there is a pair of Bi(2) atoms inside the polyhedron, as well as the pair of Y(3) atoms. This is quite similar to the 22 vertex polyhedron surrounding pairs of Be atoms in $Ru_3Be_{17}$ (Sands, Johnson, Krikorian & Kromholtz, 1962).

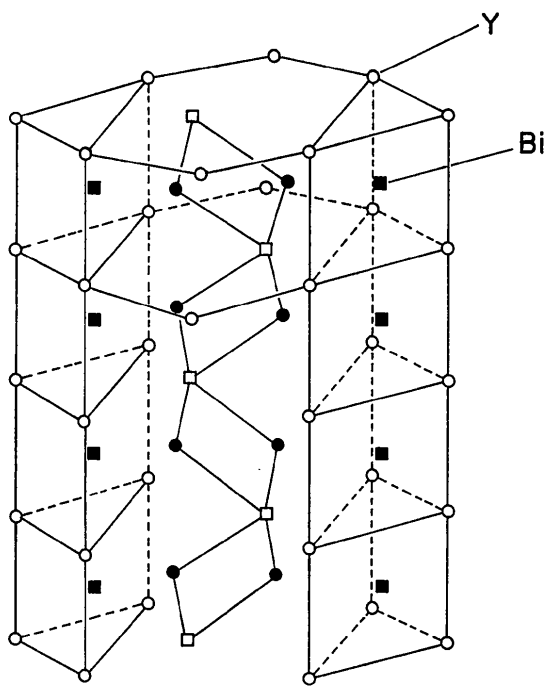


Fig. 1. A perspective view to illustrate the columns in the $Y_5Bi_3$ structure, somewhat idealized to make the trigonal and hexagonal prisms regular. Open symbols refer to atoms at $y=\frac{1}{4}$ and $\frac{3}{4}$; solid symbols to atoms at $y\simeq 0$ or $\frac{1}{2}$.

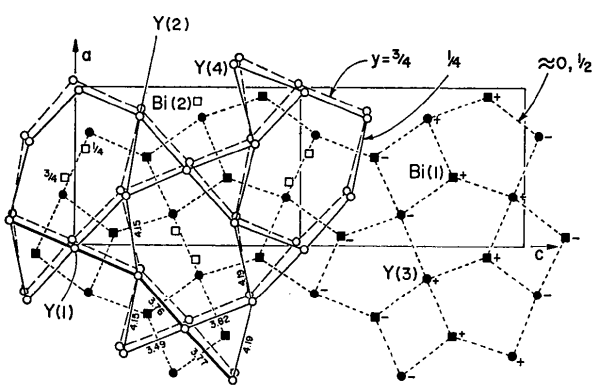


Fig. 2. The orthorhombic $Y_5Bi_3$ structure projected onto (010). The puckered diamond–pentagon network of atoms at $y\simeq 0,\frac{1}{2}$ is extended into a second cell with the ± signs to indicate displacement up or down from the $y=0$ plane.

### Comparison of $Y_5Bi_3$ and $Mn_5Si_3$ structure types

This comparison is referred to numerical values calculated for the $Gd_5Bi_3$ case where coordinates for both forms are available, using the lattice parameters of Yoshihara *et al.* (1975) for both types and the coordinates of Hohnke & Parthé (1969) for the $Mn_5Si_3$ form and the coordinates from this study for the $Y_5Bi_3$ form. There is a small increase in vol/atom in going from the $Mn_5Si_3$ to $Y_5Bi_3$ types, 29·1 to 29·6 Å$^3$, but the average CN and the average Bi–Gd and Gd–Gd distances are not appreciably changed. The significant changes are the increase in the shortest Gd–Gd distance from 3·21 [corresponding to a single bonded Gd–Gd distance, Hohnke & Parthé (1969)] to 3·39 Å and the striking increase in the average Bi–Bi distance from 3·75 Å, comparable to a metallic bonding distance, to 4·32 Å, essentially a van der Waals distance of approach.

The $Mn_5Si_3$ structure is considered to form for geometrical reasons which result in high overall coordination (Pearson, 1972). Comparison of the two types and their near neighbour diagrams (Pearson, 1972) shows that the $Y_5Bi_3$ type exhibits the same features. In the $Ln_5Bi_3$ series the $Mn_5Si_3$ type is stable with a radius ratio Ln/Bi $\gtrsim$ 1·05; at this point the Ln ion core becomes relatively no longer compressible (see below) and the $Y_5Bi_3$ type becomes the more stable form with out the short Ln–Ln single-bonded distance. The average Bi–Gd distance is not significantly different in the two structures (3·31 and 3·28 Å respectively) corre sponding to strong metallic interaction and the low CN of the nearest neighbours in trigonal prismatic arrangement. Similar constancy in the short A–B dis-

tances, associated with low CN nearest neighbour environments, is observed in the A–B distances in the $[AB_5]$ square pyramids which occur in the $AB_2$ compounds with the $SbCu_2$ and $SbLa_2$ type structures (Stassen, Sato & Calvert, 1970).

### Geometrical relationship between the $Mn_5Si_3$ and the $Y_5Bi_3$ structure types

The $Mn_5Si_3$ structure contains (in the $Gd_5Bi_3$ case) chains of $[BiGd_6]$ taper-ended trigonal 'prisms' with trigonal axes lying parallel to (0001). These face in alternate directions and have bases formed of the Gd atoms in the positions 4(*d*) $\frac{1}{3},\frac{2}{3},0$ which form ribbons parallel to **c** with the short, single-bonded, Gd–Gd distance of 3·21 Å ($=c/2$) mentioned above. When projected onto $(\bar{1}100)$ (Fig. 4) this chain of prisms is viewed end-on and it can be seen that the Bi atom centring a prism is also coordinated to 3 Gd and 2 Bi atoms in the mid-plane of the prism, thus forming an isolated, double ribbon of triangles sharing edges. This Bi coordination and the chain of alternately facing prisms can be seen in the $Y_5Bi_3$ structure running parallel to the [101] direction. The 'chain' axis has been emphasized by a heavy line in Figs. 2 and 4. For a short distance along a chain, corresponding to two prisms, the two structures can be virtually superimposed. Thus the relationship between the two can be imagined as a relaxation of the Gd–Gd chain with the Gd–Bi distances within the prism remaining virtually constant (3·31 to 3·28 Å); but as the average length of the triangle edges becomes larger (3·66 to 3·89 Å – these distances are marked on Figs. 2 and 4) the height of the prisms becomes shorter (4·91 to 4·76 Å), the chain becomes buckled and the Bi–Bi distances become much longer (3·75 to 4·5 Å). As a result of this buckling hexagonal channels can be formed. Thus the double triangle ribbon of the $Mn_5Si_3$ type becomes the diamond–pentagon network of the $Y_5Bi_3$ type. The vacant octahedral sites of the $Mn_5Si_3$ type (crosses in Fig. 4) have counterparts in the empty ends of the hexagons in the $Y_5Bi_3$ type and this brings about the speculation

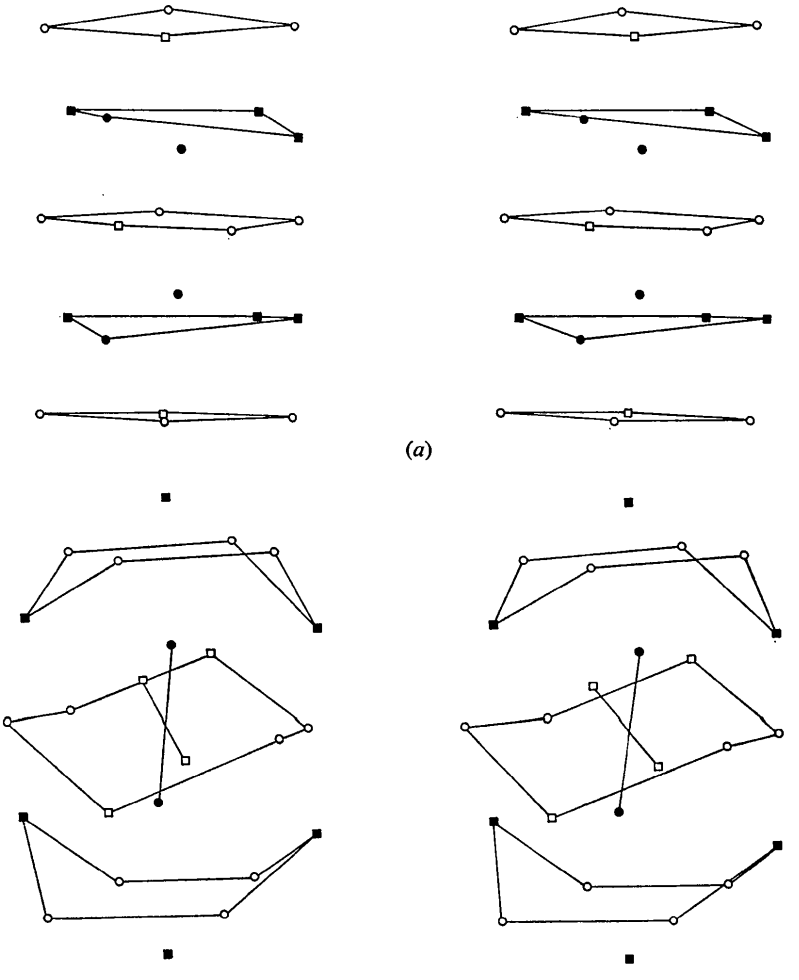

Fig. 3. (*a*) Stereo view of the polyhedron around the pair of Y(3) atoms along the *b* axis. (*b*) Stereo view of the polyhedron around the pair of Y(3) atoms and extended approximately parallel to ⟨103⟩.

that 'filled' $Y_5Bi_3$ structures may exist analogous to the filled $Mn_5Si_3$ types.

## Related structures

The general features common to the $Y_5Bi_3$ and the $Rh_5Ge_3$ structures were mentioned above. There is also a close similarity between $Y_5Bi_3$ and $Yb_5Sb_3$ which can be described as a column structure of $[SbYb_6]$ prisms forming hexagonal channels occupied by $[Yb_2Sb_2]$ rhombs (Brunton & Steinfink, 1971). A search of the literature showed that $S_5U_3$ (Potel, Brochu, Padiou & Grandjean, 1972), $Se_5U_3$ (Mosely, Brown & Whittaker, 1972), $Ca_5Sb_3$ (Martinez-Ripoll & Brauer, 1974) and $Ca_5Bi_3$ (Martinez-Ripoll, Haase & Brauer, 1974) are isostructural with $Yb_5Sb_3$ though not previously recognized as such. It may be noted that the axes ($a$ and $c$) are reversed between the $Y_5Bi_3$ and $Y_3b_5Sb$ types or if the same axial setting is used, the space group description differs. Examination shows that the (010) projections are very similar for both types, although the atoms are distributed among the site sets differently, [Yb(3) = Y(1), Yb(2+4) = Y(4+2)], the $y=\frac{1}{4}$ and $\frac{3}{4}$ layers being almost superimposable with the different space-group absences arising largely, but not wholly, from the $y\simeq 0,\frac{1}{2}$ layers which are buckled as noted in the right-hand half of Fig. 2. The relationships between the coordinates which give rise to this effect are given below where the equivalent positions in *Pnma* are compared with those in *Pcmn* for the same set of axes but with $a$ and $c$ interchanged. (The four positions related by a centre are omitted.)

| | *Pnma* *abc* | | | *Pcmn* *cba* | | |
|---|---|---|---|---|---|---|
| 1 | $x$ | $y$ | $z$ | $x$ | $y$ | $z$ |
| 2 | $\bar{x}$ | $\frac{1}{2}+y$ | $\bar{z}$ | $\bar{x}$ | $\frac{1}{2}+y$ | $\bar{z}$ |
| 3 | $\frac{1}{2}+x$ | $\frac{1}{2}-y$ | $\frac{1}{2}-z$ | $\frac{1}{2}-x$ | $\frac{1}{2}-y$ | $\frac{1}{2}+z$ |
| 4 | $\frac{1}{2}-x$ | $\bar{y}$ | $\frac{1}{2}+z$ | $\frac{1}{2}+x$ | $\bar{y}$ | $\frac{1}{2}-z$. |

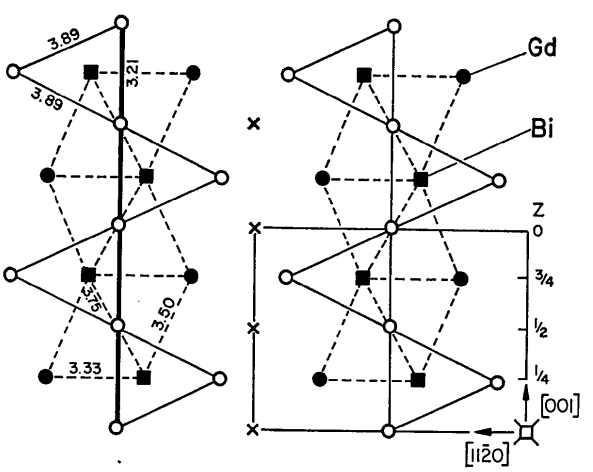


Fig. 4. A section through the hexagonal $Mn_5Si_3$ type structure of $Gd_5Bi_3$; only atoms immediately above and below are projected onto the mean plane of the section. The origin and one unit cell are outlined.

Positions 1 and 2 are unchanged whereas 3 and 4 are related by a shift of $\frac{1}{2}$ along $y$. Thus the atom networks formed by the special positions in 4($c$), are very similar in both types but the layers formed by atoms in general positions buckle in opposite senses.

## Composition

The composition of $Y_5Bi_3$ is equal or close to stoichiometric from the results of the structure analysis so that the composition difference between the $Mn_5Si_3$ and $Y_5Bi_3$ structures discussed by Yoshihara *et al.* (1975) must be a metal deficiency in the $Mn_5Si_3$ type which should therefore be reported as $Ln_{5-x}Bi_3$. This is not surprising in view of the strong compression on the Ln atoms in the 4($d$) position and the known deficiency on this site in some $Mn_5Si_3$ phases (Parthé, Jeitschko & Sadagopan, 1965).

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