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The crystal structure of Ba_4Al_5.

By MARIA L. FORNASINI, *Istituto di Chimica Fisica, Università di Genova, Corso Europa (Palazzo delle Scienze)*, 16132 *Genova, Italy*

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The compound Ba_4Al_5 has hexagonal symmetry with lattice constants $a=6{\cdot}092$ (2), $c=17{\cdot}782$ (6) Å, space group $P6_3/mmc$, $Z=2$, and $\varrho_{obs}=3{\cdot}88$ g cm^{-3}. The structure has been solved by trial methods and refined to a final R index of 0·085 for the observed reflexions. The structures of Ba_4Al_5 and the earlier determined Ba_7Al_{13} are closely related to that of the Laves phase $MgNi_2$, from which it can be geometrically derived.

Introduction

The phase 'BaAl' was first recognized by Flanigan (1952), who assigned to this compound hexagonal symmetry with $a=6{\cdot}01$, $c=17{\cdot}78$ Å. Recently these data have been confirmed in a study on the Sr–Al and Ba–Al diagrams (Bruzzone & Merlo, 1975).

The structure determination of this phase, which follows that of Ba_7Al_{13} (Fornasini & Bruzzone, 1975), completes the crystallographic study of the compounds present in the Ba–Al system.

Experimental and structure determination

The preparation of the samples has been described elsewhere (Bruzzone & Merlo, 1975). Several plate-like single crystals were examined by Laue, rotating and precession techniques. The hexagonal 6/*mmm* Laue symmetry was confirmed and the absence of *hhl* reflexions with $l=2n+1$ led to the possible space groups $P6_3mc$, $P\bar{6}2c$ or $P6_3/mmc$.

A refinement of the lattice constants was carried out at the end of the structural work on powder photographs taken with Fe $K\alpha$ radiation and gave the values $a=6{\cdot}092$ (2), $c=17{\cdot}782$ (6) Å.

The atomic sizes of Ba and Al suggest that the contents of the unit cell are Ba_8Al_{10}; this is confirmed by the pycnometric determination of the density as 3·88 g cm^{-3}, compared with the calculated value of 3·98 g cm^{-3}.

Three-dimensional intensity data from three reciprocal layers perpendicular to **a** and seven perpendicular to **c** were collected from a parallelepipedal single crystal flattened in the **c** direction (0·05 × 0·21 × 0·50 mm) using integrated precession photographs and Mo $K\alpha$ radiation. The intensities, measured with a microdensitometer, were corrected for Lorentz, polarization and absorption effects [μ(Mo) = 142 cm^{-1}] and put on common scale by inter-layer correlation, providing a group of 279 observed independent reflexions out of a total of 392 possible.

The intensities were then scaled by Wilson's method and a statistical analysis of their distribution gave a result closer to the centrosymmetric case, so that the space group $P6_3/mmc$ was chosen for the structural determination.

At this stage, as the lattice constant a of Ba_4Al_5 was comparable in numerical value with the corresponding constant a of the trigonal phase Ba_7Al_{13} ($a=6{\cdot}099$, $c=17{\cdot}269$ Å), a structure based on layers analogous to those found in Ba_7Al_{13} was assumed for Ba_4Al_5. So, using fragments of the structure of Ba_7Al_{13} and taking in account the intensity

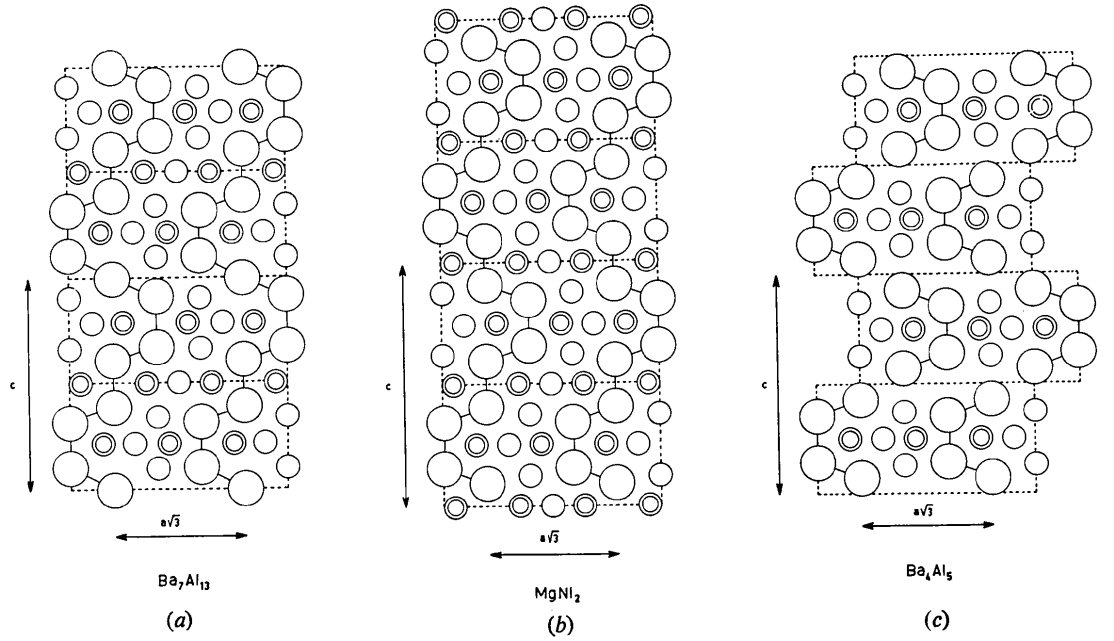

Fig. 1. Atomic arrangement in the layers parallel to the (110) plane for the three structures Ba_7Al_{13}, $MgNi_2$ and Ba_4Al_5. Large circles: Ba or Mg atoms; small circles: Al or Ni atoms; double circles: Al or Ni atoms which lie above and below the layer, respectively.

values of some reflexions, namely 008 and *hk*7, it was possible to devise a useful trial structure. A structure-factor calculation based on tentative atomic parameters gave an $R=\sum||F_o|-k|F_c||/\sum|F_o|$ of 0·134.

The least-squares refinement was then carried out with a modified version of the program *ORFLS* (Busing, Martin & Levy, 1962), using scattering factors corrected for the anomalous dispersion effect (*International Tables for X-ray Crystallography*, 1962) and giving unit weight to all observable structure amplitudes and zero weight to those unobserved. The atomic coordinates were refined with isotropic thermal parameters and one scale factor in three cycles of full-matrix least-squares calculations to an R of 0·085 for the observable reflexions. After the last cycle the average shift in the parameters was 3% of their estimated standard deviations.

The final positional and thermal parameters are listed in Table 1, and observed and calculated structure factors in Table 2.

Table 1. *Positional and thermal parameters of* Ba_4Al_5

[Space group $P6_3/mmc$ (D^4_{6h}); estimated standard deviations are given in parentheses.]

	Position	x	y	z	B (Å^2)
Ba(1)	4(*f*)	$\frac{1}{3}$	$\frac{2}{3}$	0·0700 (2)	0·55 (8)
Ba(2)	4(*e*)	0	0	0·1429 (2)	0·65 (7)
Al(1)	4(*f*)	$\frac{1}{3}$	$\frac{2}{3}$	0·6347 (18)	2·8 (6)
Al(2)	6(*h*)	0·4909 (18)	$-x$	$\frac{1}{4}$	0·7 (2)

Table 2. *Observed and calculated structure factors of* Ba_4Al_5

(An asterisk indicates reflexions too weak for measurement).

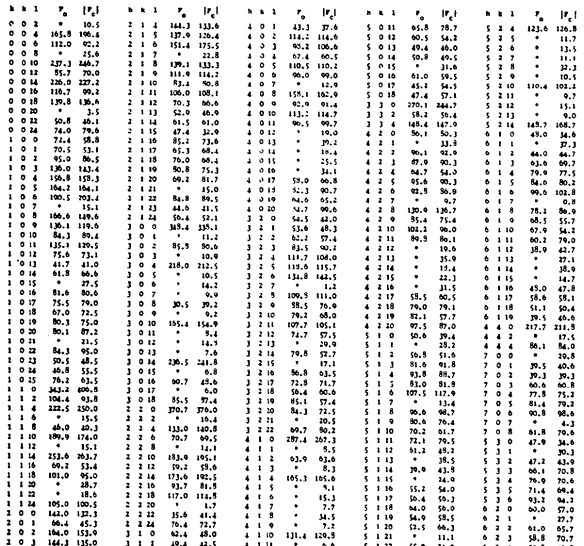

Table 3. *Interatomic distances in* Ba_4Al_5 (Å)

Ba(1)–3Ba(1)	4·31	Al(1)–1Ba(1)	3·64
–3Ba(2)	3·75	–3Ba(1)	3·70
–1Al(1)	3·64	–3Ba(2)	3·52
–3Al(1)	3·70	–3Al(2)	2·77
–3Al(2)	3·61		
		Al(2)–2Ba(1)	3·61
Ba(2)–3Ba(1)	3·75	–4Ba(2)	3·59
–1Ba(2)	3·81	–2Al(1)	2·77
–3Al(1)	3·52	–2Al(2)	2·88
–6Al(2)	3·59	–2Al(2)	3·21

Discussion

The interatomic distances of Ba_4Al_5 are listed in Table 3. As in the case of Ba_7Al_{13}, while Ba–Al and Al–Al distances have usual values, some Ba–Ba distances show appreciable contraction, nearly 15–16% with respect to the metallic radius of barium.

The atomic distribution gap criterion, already applied in other cases (Bruzzone, Fornasini & Merlo, 1970), was used to evaluate the coordination numbers of the atoms. Ba(1) and Ba(2) both have coordination number 13. Ba(1) is surrounded by three Ba(1) at 4·31 Å, three Ba(2) at 3·75 Å and seven Al ranging from 3·61 to 3·70 Å; Ba(2) is surrounded by three Ba(1) at 3·75 Å, one Ba(2) at 3·81 Å and nine Al (3·52–3·59 Å). Al(1) is coordinated with seven Ba atoms ranging from 3·52 to 3·70 Å and with three Al at 2·77 Å; Al(2) is surrounded icosahedrally by six Ba (3·59–3·61 Å) and six Al ranging from 2·77 to 3·21 Å.

As can be seen in Fig. 1, the structure of Ba_4Al_5 is closely related to those of the trigonal Ba_7Al_{13} and of the hexagonal $MgNi_2$ phases. The three structures are built up by layers parallel to the (110) plane and are characterized by the common presence of three-dimensional blocks (shown in Fig. 1 by dashed lines) with the largest atoms (Ba or Mg) arranged in a distorted tetrahedral close packing. The structure of Ba_4Al_5 can be derived from the Laves phase polytype $MgNi_2$ in the following way: (*a*) alternate blocks shift by an amount equal to $a\sqrt{3}/3$ in the [110] direction; (*b*) the Ni atoms at the boundaries of the blocks, which form kagomé nets in the $MgNi_2$ type, are removed; (*c*) the blocks approach together along the c axis. The final arrangement is shown in Fig. 1(*c*).

As already noted (Fornasini & Bruzzone, 1975), starting from the $MgNi_2$ structure, Ba_7Al_{13} also can be derived, maintaining the blocks in the same sequence and removing for each block two consecutive layers, one containing triangular nets of Mg and the other bringing kagomé nets of Ni atoms [Fig. 1(*a*)].

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