Acta Cryst. (1962). **15**, 175

Interatomic Distances in the Intermetallic Compounds $MgBe_{13}$ and $CaBe_{13}$

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(*Received* 9 *November* 1960 *and in revised form* 3 *July* 1961)

A least-squares refinement of the atomic positional parameters y and z, for the Be_{II} atoms in $MgBe_{13}$ and $CaBe_{13}$, has been carried out. This is based upon intensity measurements on polycrystalline material, using a proportional-counter diffractometer, and point-counting procedure. The treatment of measurements is discussed and a weighting scheme appropriate to counting methods is suggested.

The results obtained are:

$MgBe_{13}$: $y=0\cdot1789\pm0\cdot0010$, $z=0\cdot1143\pm0\cdot0008$
$CaBe_{13}$: $y=0\cdot1769\pm0\cdot0002$, $z=0\cdot1123\pm0\cdot0002$

The uncertainties are the calculated standard deviations.

1. Introduction

The crystal structures of the AB_{13} series of compounds is based on a face-centred cubic lattice. The space group is O_h^6–$Fm3c$, with $8A$ in $8(a)$: $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$; ------; $8B_{I}$ in $8(b)$: 0, 0, 0; ------; and $96B_{II}$ in $96(i)$; $0, y, z$; ------. Each B_{I} is surrounded by twelve B_{II} at the vertices of nearly regular icosahedron, and each A by twenty-four B_{II} at the vertices of a snub cube.

The existence of the intermetallic compounds $MgBe_{13}$ and $CaBe_{13}$ has already been reported (Baker & Williams, 1955; Elliot, Cramer & Ellinger, 1958; Sinelnikov, Ivanov & Selensky, 1958). Previous to this Baenziger & Rundle (1949) had reported a series of intermetallic compounds of composition ABe_{13}, where A is U, Th, Ce or Zr. This series was confirmed by Koehler, Singer & Coffinberry (1952). Runnalls (1954) found that a neptunium–beryllium compound approximating to $NpBe_{13}$ was face-centred cubic with a varying from $10\cdot266\pm0\cdot001$ Å to $10\cdot256\pm0\cdot001$ Å, and had reflections comparable in intensity to those from UBe_{13}.

The only metals other than beryllium reported to form compounds of the AB_{13} type are zinc and cadmium. These were originally reported by Ketelaar (1937) and subsequently investigated by Zintl & Haucke (1938). A precise determination of the interatomic distances and atomic valences in $NaZn_{13}$ was made by Shoemaker, Marsh, Ewing & Pauling (1952). Baenziger & Rundle (1949) used the values of y and z proposed by Zintl & Haucke (1938) and showed that for this structure the beryllium contributions in $ZrBe_{13}$, although small, were in the right direction to give agreement with the observed intensities. To obtain better confirmation particularly for the heavier metal compounds, Koehler *et al.* (1952) carried out neutron-diffraction studies on a powder sample of the uranium–beryllium compound. This utilized the fact that the ratio of the scattering factors of beryllium and uranium is more favourable for neutrons than for X-rays, and they concluded that although the agreement was satisfactory, some change in the parameters was indicated. The accurate determination of the parameters y and z by X-ray methods is now made more practicable because of the existence of beryllium associated with light elements in the compounds $MgBe_{13}$ and $CaBe_{13}$.

2. Preparation of the compounds

(*a*) $CaBe_{13}$

The $CaBe_{13}$ was formed by calcium reduction of the oxide (Buddery & Thackray, 1956).

(*b*) $MgBe_{13}$

The $MgBe_{13}$ was prepared by cold pressing beryllium powder at 30 tons/in.^{2}, followed by immersion in a bath of molten magnesium at 750 °C. for 30 minutes in an atmosphere of argon, with a final water quench (Williams & Jones, 1960).

The lattice parameters found for these compounds from powder photographs are:

$CaBe_{13}$ $a=10\cdot312\pm0\cdot001$ Å ,
$MgBe_{13}$ $a=10\cdot166\pm0\cdot005$ Å ,

which are in agreement with those previously reported (Baker & Williams, 1955).

3. Measurement of intensities

Measurements were made using a Philips P.W. 1050 goniometer, and Cu $K\alpha$ radiation derived from a Philips P.W. 1010 generator. The goniometer slits used were as follows; divergence, 1°; receiving, 0·1 mm.; scatter, 1°. Counting was carried out using a Twentieth Century Electronics' Xenon-filled proportional counter, connected to standard A.E.R.E. electronic equipment. Point-counting procedure was used throughout, employing standard automatic counting equipment developed by the Automatics Group at A.E.R.E., and adapted to the special requirements. Counts were made every 0·05° and varied in duration from 1 to 40 minutes, depending on the strength of the reflections. The specimens were spun in their own plane during measurement. The results in the form of counts per minute were plotted against Bragg angle, and the areas under the curves measured.

The $CaBe_{13}$ diffractometer specimen was prepared from the powder by mixing it with diluted 'Durofix' and pressing it into a holder of 18 mm. diameter and 5 mm. depth, the depth being limited by the spinning mechanism. Care was taken to ensure that the surface was flat, and it was varnished with diluted 'Durofix', because of a possible health hazard from airborne particles.

Preparatory work had shown that the sample contained appreciable quantities of CaO which could not be removed by leaching, and only $CaBe_{13}$ lines quite free from overlap with the CaO pattern were used in this investigation. Mearurements were accordingly made on 42 lines.

The $MgBe_{13}$ sample, as received, was in the form of a pellet. Glancing-angle photographs indicated the presence of free beryllium and magnesium. It was heated in vacuum to remove the magnesium, the intended treatment being 72 hours at 550 °C. By accident the temperature rose to 950 °C. for about 15 minutes. Powder photographs indicated that the sample was not damaged and that there was no observable change in the lattice parameter of the $MgBe_{13}$. Most of the magnesium had been removed.

The glancing-angle photographs also showed that some of the crystallites were large enough to introduce intensity errors. The pellet was therefore crushed and passed through a 300 mesh sieve. The powder was then made into a specimen in the same manner as the $CaBe_{13}$. This treatment did not introduce appreciable line broadening and the α_1–λ_2 doublet was still resolved. The impurities to be guarded against in this case were beryllium, beryllium oxide and magnesium. Because of overlapping, there were fewer reflections available for measurement than with the $CaBe_{13}$, and the difficulties were further increased by the relatively heavy background.

4. Tests for reproducibility of measurement

The following tests for reproducibility were made:

(*a*) Measurements carried out on a reference peak during the experimental work showed that the equipment had remained stable throughout the period, and that the results were reproducible to better than 2%.

(*b*) A second sample was prepared, and measurements were made on five of the most intense reflections. The agreement with the first sample was satisfactory.

(*c*) Diffractometer measurements showed that intensity irregularities due to large crystallites were not significant if the specimens were spun.

(*d*) Diffractometer and photographic work showed that no preferred orientation had been introduced by the method of specimen preparation.

5. Least-squares refinement of atomic positional parameters

A Ferranti 'Mercury' electronic computor was employed to carry out a least-squares refinement of the atomic positional parameters using the values obtained by Shoemaker *et al.* (1952) as the starting point. In accordance with their procedure the refinement was carried out with respect to G^2 defined as follows:

$$G_i^2(\text{calc.}) = \sum_j m_j (F_j^{\text{calc.}})^2 \tag{1}$$

$$G_i^2(\text{obs.}) = I_i^{\text{obs.}}/kLP \tag{2}$$

$$\varDelta G_i^2 = G_i^2(\text{obs.}) - G_i^2(\text{calc.}) \tag{3}$$

where m_j is the multiplicity of the jth form present in the line, L and P are the Lorentz and polarization factors, k is a scale factor and also

$$F_j^{\text{calc.}} = 2 \sum_p \hat{f}_p\,(\sin\theta_i)\cos 2\pi\,(hx_p+ky_p+lz_p) \tag{4}$$

where

$$\hat{f}_p\,(\sin\theta_i) = t_{ip} f_p\,(\sin\theta_i)\,. \tag{5}$$

$$t_{ip} = \exp\,[-B_p\,(\sin\theta_i/\lambda)^2] \tag{6}$$

$$\text{for } p=1,2 \ (p=1 \text{ for } A,\ 2 \text{ for } B)\,.$$

is a thermal vibration factor applied to each element.

The computor program was written by Mr A. R. Curtis of the Theoretical Physics Division at A.E.R.E. It provided for refinement of five parameters, namely y, z, separate thermal-vibration parameters for the two elements, and an overall scale factor on G^2_{obs}.

In a least-squares refinement the weight W_i to be assigned to each term is $1/\sigma_i^2$ where σ_i is the standard deviation of that term. For events occurring randomly in time sequence, such as the arrival of the X-ray quanta at the counter, the standard deviation of the number of events observed, N, is given by

$$\sigma N = \sqrt{N} \tag{7}$$

when a peak is superimposed upon a background, and the total counts on the peak and the background are represented by N_T and N_B respectively, the standard deviation in the peak height is given by

$$\sigma N = [N_T + N_B]^{\frac{1}{2}} \tag{8}$$

and the weight to be assigned to each reflection is

$$W_i = (N_T - N_B)^2/[(N_T+N_B)\,.\,(G^2_{\text{obs.}})^2]\,. \tag{9}$$

This applies specifically to measurements of peak height. However, if about the same number of measurements are made on each line, and about half this number are made in the background, this equation provides a useful weighting guide that can be applied to measurements of areas as well.

Table 1. *Results of refinements*

	y	z	σy	σz	R	B_1	B_2
$MgBe_{13}$	0·1739	0·1143	0·0010	0·0008	0·101	1·70	1·54
$CaBe_{13}$	0·1769	0·1123	0·0002	0·0002	0·028	0·24	0·69

6. Refinement results

The results are given in Table 1.

The atomic scattering factors used for $MgBe_{13}$ are those of James & Brindley (1931), as quoted by (Wilson, 1955), for $CaBe_{13}$ the values due to Berghuis *et al.* (1955) were used. Berghuis *et al.* (1955) do not tabulate values for un-ionised magnesium. The measurements were weighted according to equation (9).

The values of $G^2_{\text{calc.}}$ and $G^2_{\text{obs.}}$ for these refinements are given in Tables 2 and 3.

Table 2. *Intensity data for* $MgBe_{13}$

hkl	$G^2_{\text{calc.}}$ $(\times 10^{-2})$	$G^2_{\text{obs.}}$ $(\times 10^{-2})$	ΔG^2 $(\times 10^{-2})$
220	300	265	−35
222	390	389	−1
400	286	272	−14
420	1453	1465	12
622	116	124	8
444	546	537	−9
640	950	1014	64
800	441	413	−28
822 660	352	278	−74
753	515	382	−133
931	476	494	18
953	728	871	143
10,40 864	150	244	94
10,42	334	462	128
10,60 866	982	983	1
12,22 10,64	328	222	−106
11,53 975	139	139	—

7. Significance of refinement results

To assess the significance of the refinement results, additional refinements were made under the following conditions:

(*a*) With all reflections given the same weight.

(*b*) Using only the twelve reflections for which *hkl* are all odd, and to the intensities of which only the 96 Be atoms contribute.

(*c*) Using all the reflections with the exception of those used under (*b*).

In each case the values of y and z remained unchanged within the standard deviations concerned, but the values of σy, σz and R were slightly increased.

8. Discussion of refinement results

Table 3 shows that the agreement between the observed and calculated values for $CaBe_{13}$ is very good. The value for R applied to G^2 of 0·028 which corresponds to a value of 0·014 for R based on structure factors is regarded as excellent. There are several factors that contribute to this state of affairs:

Table 3. *Intensity data for* $CaBe_{13}$

hkl	$G^2_{\text{calc.}}$ $(\times 10^{-2})$	$G^2_{\text{obs.}}$ $(\times 10^{-2})$	ΔG^2 $(\times 10^{-2})$
220	1299	1309	10
222	1238	1227	−11
400	828	851	23
420	4003	4048	46
422	5113	5251	138
440	411	417	6
531	2597	2484	−113
600 442	380	395	15
620	3135	3143	8
622	842	845	3
444	1427	1439	11
640	2733	2763	29
642	4510	4408	−102
731	21	28	7
800	1002	986	−16
820 644	3610	3734	123
822 660	1535	1483	−52
751	133	130	−3
662	891	842	−49
840	1069	1091	22
753	584	571	−13
842	1117	1135	17
931	721	764	43
844	2780	2756	−24
10,00 860	168	170	2
10,2,0 862	5083	5243	160
951	699	739	39
10,2,2 666	2015	2100	85
953	1075	1127	52
10,4,0 864	1530	1530	0
10,4,2	2035	1919	−115
880	207	185	−22
11,2,1 971	406	382	24
10,4,4 882	2677	2747	70
10,6,0 866	4047	3826	−221
973	269	228	−41
10,6,2	713	684	−28
12,0,0 884	1469	1476	7
12,2,2 10,6,4	2722	2667	−54
11,5,3 975	385	371	−14
12,4,0	335	327	−8
12,4,2 10,8,0 886	1415	1291	−124

(*a*) No absorption correction has to be applied using the diffractometer method, provided that the thickness of the specimen is great enough to give maximum diffracted intensity.

(*b*) Initial measurements had shown that there was a slight but definite broadening, and under these conditions neither primary nor secondary extinction is likely to be a significant factor.

(*c*) The atoms in the crystal are nearly all of the same kind so that scattering-factor errors can be largely compensated for by adjusting the temperature factor.

(*d*) The use of a proportional counter obviated uncertainties due to the non-linearity of response of Geiger counters.

(*e*) The automatic point-counting technique enables weak reflections to be counted with accuracy.

Although from the point of view of determing y and z, $MgBe_{13}$ should represent a more favourable case than $CaBe_{13}$, the results are in fact considerably worse and this could be ascribed to the experimental difficulties, caused by the heavy background. Alternatively the accuracy could be inherently limited by some lattice defect in the compound. That the poorer results were not primarily caused by either the fewer reflections measured, or the lack of sensitivity of these reflections to changes in y and z, was shown by a further refinement on $CaBe_{13}$ using the same reflections as available for $MgBe_{13}$; y and z remained unaltered and there was only a slight increase in σy, σz and R.

A further refinement on $CaBe_{13}$ was made using the scattering factors of James & Brindley (1931) which had been used for the $MgBe_{13}$ refinement as a test in this connection. A small increase in σy, σz and R was the only effect.

Refinements on both compounds using atomic scattering factors for the ionised atoms, again gave small increases in σy, σz, and R.

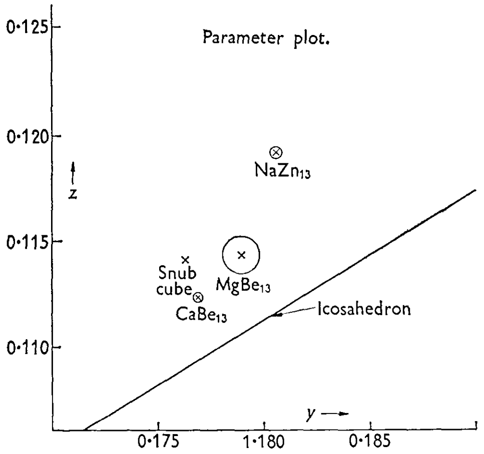

Fig. 1. Positional parameters z versus y.

9. Discussion of positional parameters results

The positional parameters y and z for $MgBe_{13}$ and $CaBe_{13}$ together with those for $NaZn_{13}$ (Shoemaker *et al.*, 1952), are plotted in Fig. 1. The radii of the circles round the points represent the standard deviation for the determination concerned. It is seen that the values of y and z for both $MgBe_{13}$ and $CaBe_{13}$ are considerably different from those of $NaZn_{13}$. The values for $CaBe_{13}$ are almost midway between the values required for the snub cube and the icosahedron. The discrepancy between the values for the $CaBe_{13}$ and the $MgBe_{13}$ are larger than would be expected from the standard deviations involved, so that this difference may be real. On the other hand both this difference and the larger error for the $MgBe_{13}$ could be explained by a defect in the lattice of this sample of the compound.

Table 4. *Bond lengths in* $MgBe_{13}$

Bond to atom	D	σ
A. Bonds involving Be_{II} $(0, 0, 0)$		
Be_{II} $(0, y, z)$	2·158 Å	0·009 Å
B. Bonds involving Be_{II} $(0, y, z)$		
Be_{II} $(0, z, \frac{1}{2}-y)$	2·201	0·012
Be_{I} $(0, 0, 0)$	2·158	0·009
Be_{II} $(z, \frac{1}{2}-y, 0)$	2·188	0·018
Be_{II} $(z, 0, y)$	2·256	0·009
Be_{II} $(0, y, \bar{z})$	2·324	0·016
Mg $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	2·980	0·009
C. Bonds involving Mg $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$		
Be_{II} $(0, y, z)$	2·980	0·009

Table 5. *Bond lengths in* $CaBe_{13}$

Bond to atom	D	σ
A. Bonds involving Be_{I} $(0, 0, 0)$		
Be_{II} $(0, y, z)$	2·161 Å	0·002 Å
B. Bonds involving Be_{II} $(0, y, z)$		
Be_{II} $(0, z, \frac{1}{2}-y)$	2·274	0·003
Be_{I} $(0, 0, 0)$	2·161	0·002
Be_{II} $(z, \frac{1}{2}-y, 0)$	2·226	0·004
Be_{II} $(z, 0, y)$	2·261	0·002
Be_{II} $(0, y, \bar{z})$	2·316	0·004
Ca $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	3·038	0·002
C. Bonds involving Ca $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$		
Be_{II} $(0, y, z)$	3·038	0·002

10. The bond lengths

The bond distances for these compounds are given in Tables 4 and 5. Shoemaker *et al.* (1952) found that in $NaZn_{13}$ the distance from Zn_{I} to each of the twelve Zn_{II} around it was 2·659 Å, a value very close to the value 2·660 Å found for the six shorter ligates around a given zinc atom in zinc itself. This situation does not exist in the beryllium compounds where values of

2·161 Å for the calcium compound and 2·158 Å for the magnesium compound, although in agreement with each other to the extent of the standard deviations, are far removed from either of the values of 2·225 Å or 2·286 Å for beryllium. Some of the other bond distances however are close to values for beryllium or to each other. In particular the value 2·226 Å for the bond length involving $Be_{II}(0, y, z)$ and Be_{II} $(z, \frac{1}{2}-y, 0)$ in $CaBe_{13}$ is very close to the former.

The author's thanks are due to Dr H. M. Finniston, now of the Nuclear Power Plant Company, and to Mr J. Williams of the Metallurgy Division, A.E.R.E., for their interest and encouragement; and to Mr A. R. Curtis and Mr E. B. Fossey of the Theoretical Physics Division, A.E.R.E., for valuable discussion concerning the computation.

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Acta Cryst. (1962). **15**, 179

Structures Cristallines de Deux Variétés Allotropiques de Manganite de Baryum. Nouvelle Structure ABO_3

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(*Reçu le* 2 *juin* 1961 *et révisé le* 27 *juin* 1961)

$BaMnO_3$ at low temperature is hexagonal from the type $BaNiO_3$. The space group is C_{6v}^4, the parameters are $a=5{\cdot}672$ and $c=4{\cdot}71$ Å. There are two ABO_3 units in a unit cell. $BaMnO_3$ at high temperature belongs to the space group D_{6h}^4 with $a=5{\cdot}669$ and $c=9{\cdot}38$ Å. The hexagonal unit cell has four sample ABO_3 units. The lattice is constituted by layers of composition BaO_3 in a close-packed arrangement of atoms, like the one of the perowskite, but with a sequence *ABAC*.

Les composés, de formule générale ABO_3, dérivés du type perowskite ont fait l'objet de nombreux travaux. Les différentes structures mentionnées correspondent à 1, 2, 6, 8 ou même davantage de motifs ABO_3 par maille.

Burbank (1948) envisage toutefois la possibilité d'une structure à 4 motifs.

$BaMnO_3$ de basse température

Le manganite $BaMnO_3$ de basse température a été préparé suivant une méthode analogue à celle de Scholder (1952), par thermolyse du manganate $BaMnO_4$. La réaction est complète dès 400 °C. (Hardy, 1961). Nous avons vérifié oxydimétriquement que le manganèse répond à la valence 4 dans le produit formé.

L'étude radiocristallographique a été faite avec le rayonnement α du fer sur le produit pulvérulent. La similitude des diagrammes X montre que $BaMnO_3$ de basse température est un isotype de $BaNiO_3$ dont la structure a été établie par Lander (1951). Le groupe d'espace est $P6_3mc$, C_{6v}^4; les paramètres de la maille hexagonale ont pour valeurs:

$$a=5{,}672\pm0{,}004,\quad c=4{,}71\pm0{,}01\ \text{Å}$$

d'où:

$$c/a=0{,}830\ .$$

La présence de 2 motifs $BaMnO_3$ dans la maille donne une densité X ($d_x=6{,}01$ g./ml.) très voisine de la densité observée au picnomètre ($d=6{,}06\pm0{,}10$ g./ml.).

L'atome de manganèse se trouve en position (*a*)