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The Structure of *T*(AlFeBe)

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The crystal structure of an intermetallic compound with formula $FeAl_2Be_{2.3}$ has been determined by single-crystal methods. It is a Laves phase of the $MgCu_2$ type, with the iron and beryllium ordered in the copper sites of $MgCu_2$ so that the symmetry is reduced from cubic to monoclinic. The interatomic distances are consistent with those found in other beryllium compounds and there is no evidence that electron concentration is an important factor for this structure. The crystals frequently occur as twins; this is discussed in terms of the proposed structure.

1. Introduction

In a recent survey of ternary alloys formed by aluminium, transition metals and divalent metals, Raynor, Faulkner, Noden & Harding (1953) have presented results on the iron–aluminium–beryllium system. Alloys in the range 0–5 wt. % Be and 0–6 wt. % Fe were used. A ternary compound was found which has a surface of primary separation lying between those of $FeAl_3$ and beryllium and which enters into equilibrium with the α solid solution. It was not easy to identify the phase micrographically, but, on extraction, the crystals could be distinguished from those of $FeAl_3$ as they are approximately regular polyhedra, in contrast to the plates and needles of the binary compound. The composition of a sample of extracted crystals was obtained by Faulkner (1953). In atomic percentages, it corresponds to 17·9% Fe, 38·9% Al and 43·2% Be, indicating an approximate formula $FeAl_2Be_{2.3}$.

2. Experimental data

Details of this work can be found in a thesis (Black, 1954). Although the various crystal forms observed suggested cubic or hexagonal symmetry, the Laue symmetry found was $2/m$, with a systematic absence indicating C-face centring of the monoclinic cell. The cell dimensions, measured using a Farquhar–Lipson (1946) camera, were:

$$a = 7{\cdot}718\pm0{\cdot}003,\quad b = 4{\cdot}4554\pm0{\cdot}0004,$$
$$c = 4{\cdot}542_4\pm0{\cdot}003\ \text{Å};\quad \beta = 124^\circ\ 32'\pm2'.$$

The density, measured by a flotation method, is $3{\cdot}47\pm0{\cdot}03$ g.cm.$^{-3}$, and this means that there can be 2·10 units of $FeAl_2Be_2$ to the cell, or 1·98 units of $FeAl_2Be_3$.

Intensity data were collected on Weissenberg photographs with filtered molybdenum radiation, using a multiple-film technique. The intensities were measured by visual comparison with a standard scale, and were corrected for Lorentz and polarization factors and approximately for absorption, using the Bradley (1935) tables for a cylindrical specimen.

3. Analysis of the structure

The space group $C2/m$ was assumed, and this fixes the heavy (iron) atom at the origin. The phases of all but the weakest reflexions were then fixed by the iron-atom contribution, and refinement by means of one- and two-dimensional syntheses of F_o and (F_o-F_c) then served to determine the positions of the other atoms. The final R factor on 175 $(h0l)$ structure factors was 0·069. Details of the solution, and a list of F_o and F_c data, are available elsewhere (Black, 1954). It was deduced from the Fourier syntheses that the beryllium site (f) is about 75% occupied. This is in agreement with the chemical analysis and density measurement, which indicate a deficiency of beryllium corresponding to approximately 65% occupation of the site.

The final positions and parameters are:

Space group: $C2/m$.

2 Fe in 2(*a*):	$0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, 0.$
4 Al in 2(*i*):	$x, 0, z;\ \bar{x}, 0, \bar{z};\ x+\frac{1}{2}, \frac{1}{2}, z;\ \bar{x}+\frac{1}{2}, \frac{1}{2}, \bar{z};$ with $x = 0{\cdot}3707,\ z = 0{\cdot}1139.$
3·0 Be in 4(*f*):	$\frac{1}{4}, \frac{1}{4}, \frac{1}{2};\ \frac{1}{4}, \frac{3}{4}, \frac{1}{2};\ \frac{3}{4}, \frac{3}{4}, \frac{1}{2};\ \frac{3}{4}, \frac{1}{4}, \frac{1}{2}.$
2 Be in 2(*c*):	$0, 0, \frac{1}{2};\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}.$

The probable errors in the parameters of the aluminium atom were investigated using the formulae of Booth (1946) and Booth & Britten (1948), which are based on different assumptions (Lipson & Cochran, 1953). These give a mean value of 0·001 Å for $\sigma(x)$. Interatomic distances Al–Al, Fe–Al and Be–Al have standard errors of 0·002 Å; for distances between atoms in special positions the error is 0·0015 Å, and is due to the error in measured cell dimensions.

4. Discussion

(i) *Description of the structure*

A plan of the atomic positions is shown in Fig. 1. In describing the overall pattern, Fe and Be atoms may

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be treated as equivalent because of their similar sizes and coordinations. Parallel to the (002), (220), ($\bar{2}$20) and ($\bar{4}$02) planes, alternate planes of atoms are flat and have the pattern of a close-packed layer with an

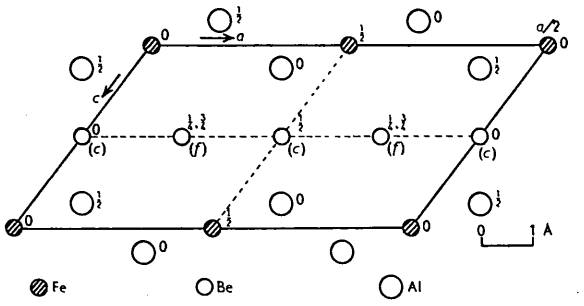

Fig. 1. Atomic positions in a unit cell shown in projection down the [010] direction. Fractional y parameters are indicated.

ordered vacancy of one-quarter of the sites. The angles between these planes are all within 1·5° of the angle 70° 32′, the angle between {111} planes in a face-centred cubic structure. The monoclinic a, b and c axes correspond to [$\bar{2}$11], [011] and [0$\bar{1}$1] directions in a cubic cell, where the poles of the above planes are [111] directions. For example, the angle between [$\bar{2}$11] and [0$\bar{1}$1] cubic directions is 125° 16′, compared with the measured β angle of 124° 32′. Comparison of the structure with a face-centred cubic structure reveals a simple relationship. Half of the sites of a face-centred cubic pattern are occupied by atoms arranged in tetrahedra which share corners but not faces or edges. This is the pattern of Fe and Be atoms, with the Fe's so distributed that there is one to each tetrahedron and that contact between Fe atoms is avoided. The remaining (vacant) sites of the face-centred cubic pattern form a similar set of tetrahedra; an Al atom is placed at the centre of each of these tetrahedra. There is then one Al per two sites, so that the ratio of Al to other types of atom is 1:2 and the larger Al atom is accommodated without strain. This is a well known structure, the $MgCu_2$-type of Laves phase. As far as the author is aware, its derivation from a close-packed cubic structure has not previously been given in the above form.

(ii) *Interatomic distances and coordinations*

These are given in Table 1 and the mean values are reviewed in Table 2.

The coordination of Fe and Be atoms can be seen in Fig. 2(a). Each Fe atom is at the centre of a hexagon of Al atoms whose members lie alternately above and below the C face of the cell, being displaced from this plane by ±0·4 Å. The Be neighbours then form two antipodal triangles in the planes midway between the C faces. This is the coordination of a close-packed structure, except that the six-membered ring is puckered to increase the separation of its members from

Table 1. *Interatomic distances*

Atom	Neighbour	No. of neighbours*	Distance (Å)
Fe	Be(f)	4	2·270
	(c)	2	2·271
	Al	4	2·610
		2	2·603
Al	Fe	2	2·610
		1	2·603
	Al	2	2·706
		1	2·719
		1	2·882
	Be(c)	1	2·633
	(f)	2	2·636
	(c)	2	2·656
	(f)	2	2·652
	(f)	2	2·660
Be(f)	Fe	2	2·270
	Al	2	2·652
		2	2·636
		2	2·660
	Be(f)	2	2·228
	(c)	2	2·228
Be(c)	Fe	2	2·271
	Al	2	2·633
		2	2·656
	Be(f)	4	2·228

* In these numbers, no allowance is made for the fact that Be(f) sites are only 75% occupied.

Table 2. *Mean interatomic distances*

	Mean distance (Å)	Goldschmidt distance (Å)
Fe–Al	2·608	2·65
Al–Al	2·753* / 2·710†	2·82
Al–Be	2·649	2·54
Fe–Be	2·270	2·37
Be–Be	2·228	2·25
Fe–Fe	4·50	—

* All four. † Shorter three.

each other and to enable the other atoms to be closer to the central atom than these six. The environment of the Be(f) atom is similar, with one opposing pair of the Be(f) atoms in Fig. 2(a) replaced by Fe atoms, whilst the environment for Be(c) is obtained by replacing the Be(c) of Fig. 2(a) by Fe atoms.

The Al coordination can also be described in terms of layers parallel to the C face; Fig. 2(b) is a projection on this face. The central Al lies 0·4 Å above the face and has three Fe neighbours in the face and three Al's below it, spaced alternately round a hexagon. The Be then lies above in a hexagon and below in a triangle. There is a fourth Al neighbour, which is a mirror image of the central atom in the plane of the beryllium hexagon; the distance of this latter is large (2·88 Å) compared with the mean of the other three (2·71 Å).

The Fe–Al distance found in this structure is contracted with respect to the Goldschmidt radii, but if Al is given a radius corresponding to the mean inter-

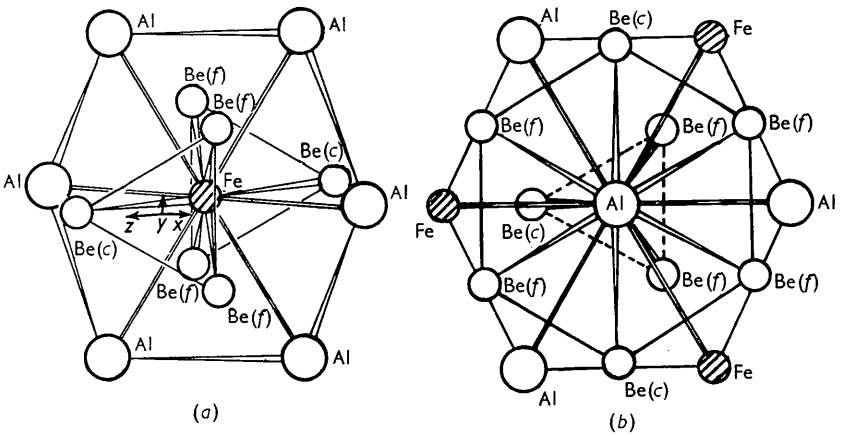

Fig. 2(*a*). Co-ordination of iron atom. Contacts of neighbours in planes parallel to the *x*–*y* plane are indicated.
(*b*) Co-ordination of aluminium atom shown in projection down the [001] direction. Atoms in contact at the same height are joined by full or broken lines.

aluminium distance in this structure, the contraction is accounted for. The inter-beryllium distance (2·228 Å) corresponds to the shorter of the two distances (2·221 Å and 2·281 Å) found in pure beryllium (Owen & Pickup, 1935). If Be is given the smaller radius, the Be–Al distance is longer than the sum of the radii in this structure (i.e. Be = 2·23/2, Al = 2·75/2 Å) by 6%. The Fe–Be distance is shorter than the sum of the appropriate Goldschmidt radii by 4%. This might be compared with the contraction of aluminium–transition-metal distances in aluminium-rich compounds (see Taylor, 1954), but comparison with other beryllium compounds suggests another interpretation.

Binary Laves phases formed with beryllium have been studied by Misch (1935*a*, *b*, 1936). Iron and beryllium form two Laves phases. In one of these, $FeBe_2$, which has an $MgZn_2$-type structure, the distance between Be atoms varies from 2·085 Å to 2·106 Å. The Fe–Fe distance is about 2·55 Å, and the Fe–Be distances lie between 2·380 and 2·451 Å. In $FeBe_5$, with an $MgCu_2$-type structure, the large atom sites are occupied by a disordered distribution of Fe and Be atoms, so that the formula may be written $2\,(Fe_{0.5}Be_{0.5})Be_2$. The shortest inter-beryllium distance is 2·09 Å. In $PdBe_5$ and $AuBe_5$ the distribution is similar, but the lattice of large atoms is ordered with the Be and Pd or Au atoms lying on a zinc-blende pattern. In the present structure, if Be is given the short radius that it exhibits in these structures, then the short Fe–Be distance is accounted for. Thus each Fe atom is in close contact with its Al and Be neighbours, but the Be's are not in close contact with each other or with the Al's. Subject to a minimum radius of 1·05 Å, the packing conditions for Be atoms in these structures do not seem to be critical; in both $AuBe_5$ and $PdBe_5$ phases, distances between the Be and the larger atoms appear to be contracted with respect to the pure metal radii, but are accounted for by a smaller Be radius, which is directly observed in those structures where the Be is more closely packed.

Both $PdBe_5$ and $AuBe_5$, in which atoms are ordered on the large-atom sites, can be obtained in the disordered state. The specimens examined in the present work (where Fe and Be are ordered on the small-atom sites) were obtained by slow cooling, and it is not known whether a disordered phase can be found. There are two other compounds, UNi_5 and UCu_5 (Baenziger, Rundle, Snow & Wilson, 1950), which form $MgCu_2$-type structures with ordering of the type found in these beryllium compounds. It is not easy to analyse these distances in terms of Raynor & Berry's (1953) discussion of interatomic distances in the $MgZn_2$- and $MgCu_2$-type phases. The results do not fit either of the linear series deduced for AB_2 binary compounds with Fe or Be as B components.

(iii) *Electron counts and Brillouin zone*

Aluminium-rich transition metal compounds have been considered by other workers as electron compounds, and attention has been directed to their Brillouin zone characteristics and to the possibility of electron transfer into transition metal (3*d*) shells (for a critical survey see Taylor, 1954).

The results of counts on F_o and (F_o-F_c) syntheses of the $(h0l)$ projection of this structure are given in Table 3. The observed F's have not been placed on an absolute scale by experimental measurements, and the F_o coefficients were scaled by comparison with F_c coefficients. For the latter, the Fermi–Thomas scattering factor for iron and the James & Brindley

Table 3. *Review of electron counts*

Atom	F_o synthesis	F_o-F_c synthesis
Fe	30·8	+1·0
Al	11·9	−0·8
Be(*f*)	4·5 (3·0)	0·0
Be(*c*)	2·8	+2·3

The F_o counts assume zero electron density between atoms and are then scaled to give the correct total per unit cell. Be(*f*) corresponds to 1·5 atoms and the count per atom is given in brackets.

scattering factor for normal aluminium were used. Effects shown in the F_o syntheses are not confirmed in the (F_o-F_c) syntheses. A reasonable explanation for the count of +2·3 on Be(c) has not been found and any attempt to interpret the other smaller effects could hardly be justified.

The structure factors for all planes of $\sin\theta/\lambda \leqslant 0{\cdot}35$ were calculated. There is no set of very strong reflexions which would form an approximately spherical Brillouin zone. The closest of the very strong planes [the (020) and $(\bar{3}11)$] would limit a Fermi sphere to contain 1·11 electrons per atom, which must be much less than the number of electrons per atom for $FeAl_2Be_{2\cdot3}$, even if iron absorbs 2·66 electrons according to the hypothesis of Raynor (1949).

(iv) *Twinning*

Some of the crystals examined were twins, and the diffraction data show that the two individuals of a twin are related by reflexion across a $(\bar{2}01)$ plane. One possible atomic arrangement was found to satisfy this condition and to give a reasonable atomic distribution over the composition plane. This is shown in Fig. 3. The Fe atom on the composition plane has the same numbers of Al and Be atoms at the same distances as other Fe atoms, but their relative arrangement is changed. The Be atom has the same numbers of different types of neighbours but not the same set of distances. The only effect for atoms not on this plane is the change in Al contact distance p–q (Fig. 3) from $2{\cdot}71_9$ Å to $2{\cdot}68_1$ Å. If alternation of twin components occurred frequently, extra diffuse reflexions would be expected: no trace of these has been found.

A plot in reciprocal space of the very strong reflexion planes shows that these are brought into approximate coincidence by the twinning (see also Fig. 2 of Robinson (1952), and Black (1954)). This implies that the prominent layers of atoms in one component are parallel to similar layers of similar spacing in the other.

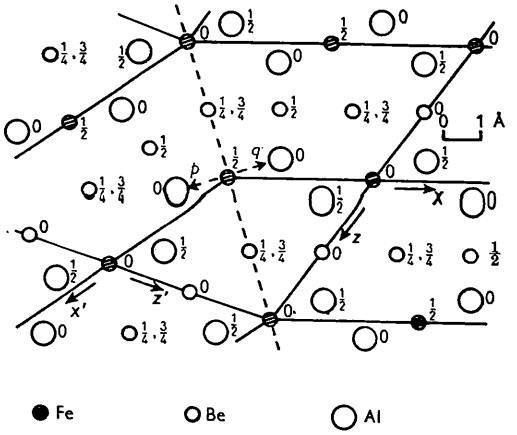

Fig. 3. Projection down the [010] direction to show the junction of twin components. The broken line is the composition plane across which the components are related by reflexion.

5. Conclusion

The Laves structures are regarded as a mode of packing of atoms whose radii are in the ratio 1:1·225. It has been shown that the behaviour of some ternary magnesium phases can be explained by assuming that changes in electron:atom ratio are also important (Raynor, 1949). The present structure can be described in terms of a normal packing of the different atoms if it is assumed that beryllium atoms have a minimum radius of 1·05 Å, an assumption that is confirmed by the evidence of other beryllium compounds. There is no pronounced contraction of the Fe–Al distances. Analysis in terms of Brillouin-zone effects is not possible and electron-transfer effects, if any, must be quite small. This phase cannot, therefore, be classified with the aluminium-rich transition-metal compounds.

The deficiency of beryllium, which appears to be localized on one particular site, is not explained, and the possibilities of a variable composition and of a disordered state remain to be investigated. In the only comparable ternary system studied, Al–Be–Mn (Raynor *et al.*, 1953), a compound of this type has not been found; there is a binary $MnBe_2$ Laves phase, but no phase comparable with $FeBe_5$.

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