

STRUCTURAL ANALYSIS OF LAVES PHASES WITH Ti

M. J. M. DE ALMEIDA, M. M. R. COSTA, L. ALTE DA VEIGA,
L. R. ANDRADE and A. MATOS BEJA

Grupo de Estruturas dos Materiais, FC1, INIC, Departamento de Física,
3000 Coimbra, Portugal

(Received 29 December 1980)

ABSTRACT — The atomic structure of the Laves phases TiFe_2 and TiMn_2 has been refined by X-ray diffraction from single crystals. The interatomic distances have been calculated and discussed in terms of the contraction of atoms in these structures.

1 — INTRODUCTION

A detailed description of the structures of the Laves phases has been given by Sinha [1] based on the original work of Laves and Witte [2].

These phases have generally a stoichiometric composition AB_2 and the closest packing of the constituent atoms occurs when the ratio of their atomic radii, R_A/R_B , is 1.225. If we consider that two atoms make a 'contact' when their interatomic distance is smaller than the sum of the corresponding atomic radii, then, under the above conditions, only A-A and B-B contacts are possible.

However, several binary alloys with a Laves phase structure for which R_A/R_B deviates from that ideal value have been found, R_A/R_B varying between 1.05 and 1.68. In these cases, adjustments in the atomic dimensions can be observed, so as to preserve the closest possible packing of the atoms in the structure; these can possibly be attributed to changes in the valences of the constituent elements. Thus, when $R_A/R_B > 1.225$ the A atom and hence the interatomic distance A-A undergo an apparent contraction [3]. In some of these Laves phases Pearson [4] has observed the occurrence not only of

A-A and B-B but also of A-B contacts. When $R_A/R_B < 1.225$, B-B contacts are predominant.

Values of R_A/R_B favouring the structure of the Laves phases occur frequently when A is a transition metal to the left of chromium in the periodic table and B is an element to the right of this metal, either in the same or in a different series.

The structural study of three Laves phases, $TiMn_2$, $TiFe_2$ and $TiCo_2$ was undertaken in this Laboratory. In the present paper the results obtained by X-ray diffraction for the two first alloys are reported. The aim of this work is the accurate determination of interatomic distances and the analysis of their variation in a set of AB_2 alloys whose B atom varies along a transition series in the periodic table.

2—EXPERIMENTAL

The Laves phases are homogenous over the ranges 22.5–35.0 at% Ti (Murakami *et al*, [5]) and 31.6–42.0 at% Ti (Murakami *et al*, [6]), respectively.

Both phases have the $MgZn_2$ (C14) hexagonal type structure. Ingots of $TiFe_2$ and $TiMn_2$, containing both 33.33 at% Ti were kindly supplied by Dr. M. Nevitt, Argonne National Laboratory, Illinois, U. S. A..

Single crystals of $TiFe_2$ and $TiMn_2$ with regular shape and dimensions of the order of 0.2 and 0.4 mm, respectively, were selected for the subsequent diffraction experiments.

The lattice parameters obtained by the method of Farquhar and Lipson [7] for the specimen of $TiFe_2$ are:

$$a = 4.7942 \pm 0.0003 \text{ \AA} \quad c = 7.8238 \pm 0.0003 \text{ \AA} \quad c/a = 1.632$$

Measurements of the lattice parameters of both crystals were carried out in an automatic 4-circle diffractometer, yielding the results:

$$TiFe_2: \quad a = 4.7870 \pm 0.0004 \text{ \AA} \quad c = 7.8150 \pm 0.0007 \text{ \AA} \quad c/a = 1.633$$

$$TiMn_2: \quad a = 4.8310 \pm 0.0005 \text{ \AA} \quad c = 7.9390 \pm 0.0008 \text{ \AA} \quad c/a = 1.643$$

No reason could be found for the significant difference in the lattice parameters of $TiFe_2$ obtained by the two methods.

A preliminary study of both structures, based on Laue and oscillation photographs, has justified the choice of the spatial group $P6_3/mmc$ attributed to both structures; this is in agreement with previous investigations (Wallbaum, [8]; Duwez and Taylor, [9]).

The integrated intensities of a large number of reflections from both crystals were collected, using filtered Mo-K α radiation, on a Philips automatic diffractometer of the Instituto de Química-Física «Rocasolano» of the Consejo Superior de Investigaciones Científicas, Madrid (Spain).

A set of independent $0k.l$ reflections from either crystal out to $(\sin \theta)/\lambda = 1.15 \text{ \AA}^{-1}$ were selected; of these, approximately 100 from TiFe_2 and 86 from TiMn_2 , for which $F_o > 3\sigma_{F_o}$ were used in subsequent structure refinements, F_o and σ_{F_o} standing for the observed structure factor amplitude and the corresponding standard deviation.

3 — STRUCTURE REFINEMENT

The atomic positions in the hexagonal unit cell of the C14 type of structure can be determined using the reflection intensities from the zero layer line of the $[\bar{2}1.0]$ projection.

For simplicity, a non-primitive orthorhombic unit cell with dimensions a , $a\sqrt{3}$ and c was chosen, which is equivalent to the primitive hexagonal cell; hence, the hexagonal indices $0k.l$ were transformed into orthorhombic indices, $02k.l$.

The reflection intensities were corrected in the usual way for Lorentz and polarization factors. Allowance was made for the resolution of the $\alpha_1 \alpha_2$ doublet by scaling observed and calculated structure factor amplitudes, F_o and F_c , in regions of $(\sin \theta)/\lambda$. This procedure also takes into account the variation of absorption in the crystal: owing to the regular shape and small dimensions of both TiFe_2 and TiMn_2 specimens no further absorption correction was applied.

Atomic scattering factors were calculated from the set of analytical constants given by Forsyth and Wells [10] for Fe, Ti^{2+} and Mn^{2+} .

The refinement of atomic and temperature parameters was based on two-dimensional Fourier syntheses, $(F_o - F_c)$; the atomic parameters x and z known for the MgZn_2 structure were initially postulated in both cases. The final stages of the refinement will now be described for TiFe_2 and TiMn_2 separately.

TiFe₂

An isotropic temperature factor, $B = 0.439$, obtained by the Wilson method, was used for the calculation of F_o in the first Fourier syntheses. The refinement of this factor was carried out in the following way: values of B , varying between 0.3 and 0.5 were attributed to the iron and titanium atoms separately, while the atomic parameters were kept fixed. The best difference maps and lowest R-factors were obtained for the value initially postulated for B .

In the final stages of the refinement, extinction was found to affect two of the strongest reflections, namely 400 and 401. An empirical extinction correction (Damjanovick and Black, [11]) was applied. The Fourier difference maps did not evidence any significant alteration and the R-factor decreased from 0.054 to 0.052.

The final values of the atomic parameters, their standard deviations and temperature factors are shown in table 1, together with the corresponding R-factor. Figures 1(a) and 1(b) show the final F_o and $(F_o - F_c)$ maps.

Table 1 — Atomic parameters and their standard deviations, temperature factors and R-factors for the structures TiFe₂ and TiMn₂.

Position	Atom		MgZn ₂ (AB ₂)	TiFe ₂ (AB ₂)	TiMn ₂ (AB ₂)
2 (a) (0, 0, 0)	B	—	—	—	—
6 (h) (x, 2x, 1/4)	B	x	0.1667	0.1710 ± 0.0002	0.1701 ± 0.0004
4 (f) (1/3, 2/3, z)	A	z	0.0625	0.0640 ± 0.0003	0.0642 ± 0.0005
				B _{Ti} = 0.439	B _{Ti} = 0.50
				B _{Fe} = 0.439	B _{Mn} = 0.30
				R = 0.052	R = 0.051

TiMn₂

An isotropic temperature factor, $B = 0.4$, was initially used in the calculation of F_o . The Fourier difference maps were found to be sensitive to variations of this value, and suggested the use of different temperature factors for Ti and Mn.

No extinction correction was applied to the reflection intensities, since the observed structure amplitudes, F_o , were not significantly lower than the corresponding F_c , even for the strongest reflections.

The refined atomic parameters, their standard deviations and the temperature factors, as well as the corresponding R-factor, are listed in table 1. Figures 2(a) and 2(b) show the final F_o and $(F_o - F_c)$ maps.

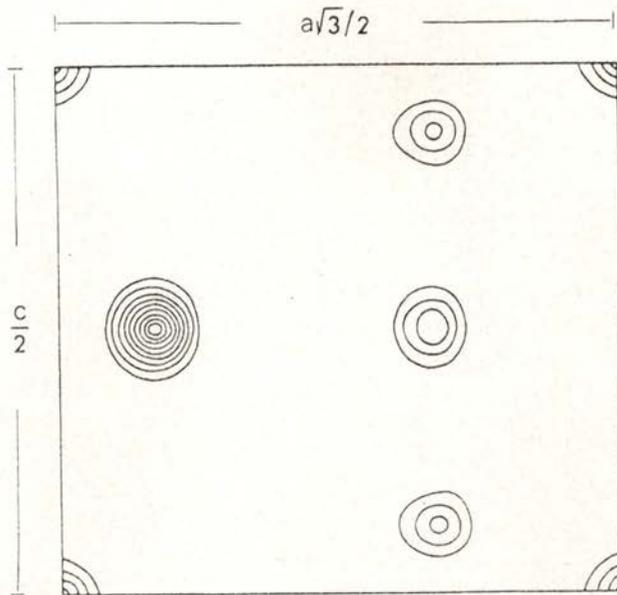
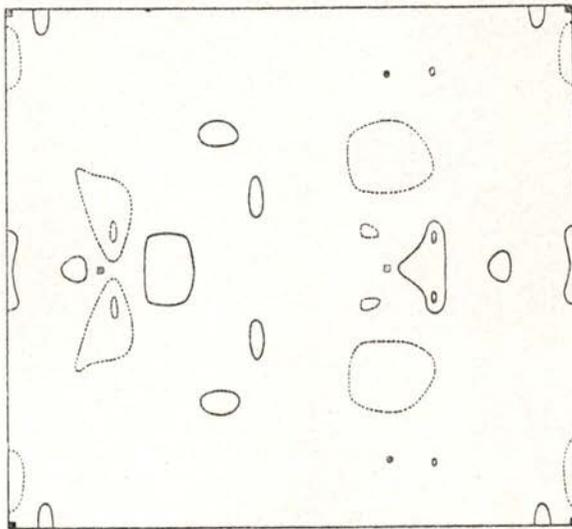


Fig. 1 — Fourier syntheses for the $[2\bar{1}0]$ projection of TiFe_2 .
 (a) F_0 ; contours are at arbitrary equal intervals;



(b) $(F_0 - F_c)$; contours at 1/15 those of F_0 ; dashed lines represent negative contours;
 ■ positions occupied by Ti atoms
 • positions occupied by Fe atoms

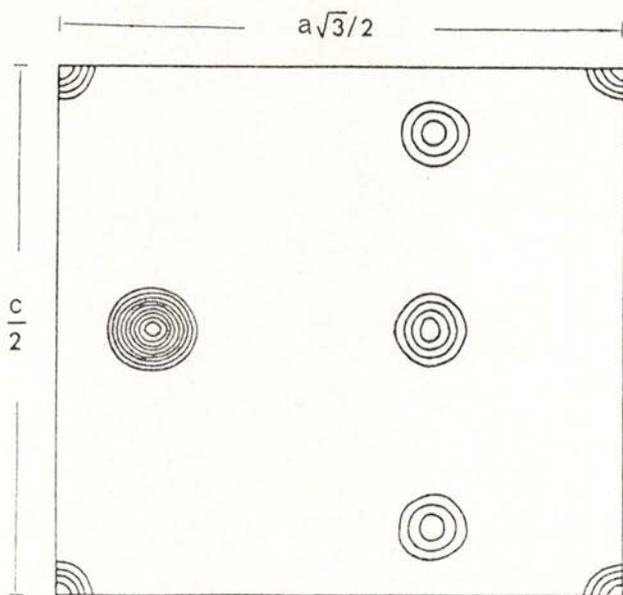
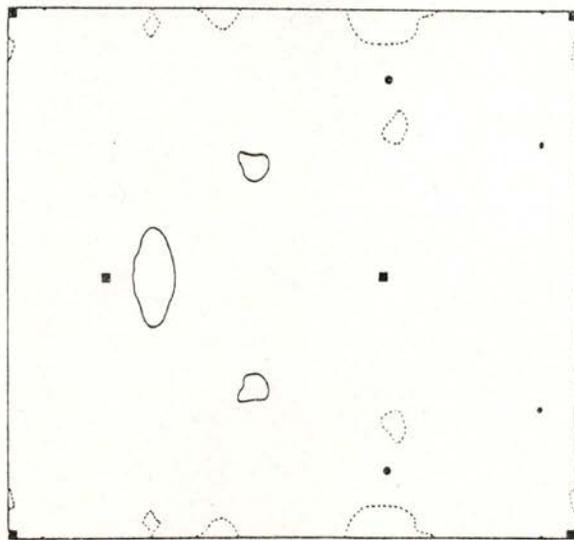


Fig. 2—Fourier syntheses for the $[2\bar{1}0]$ projection of TiMn_2 .
(a) F_0 ; contours are at arbitrary equal intervals;



(b) $(F_0 - F_c)$; contours at $1/10$ those of F_0 ; dashed lines represent negative contours;
 ■ positions occupied by Ti atoms
 • positions occupied by Mn atoms

4— CONCLUSIONS

The atomic radii of the constituents of binary transition metal alloys with the $MgZn_2$ type structure are in general markedly different. This fact, together with the occurrence of compositions very close to the stoichiometry, suggests that these structures should be fully ordered; the lack of experimental results confirming such conclusion has been pointed out by Sinha [1].

The order of magnitude of the reliability factors, as well as the Fourier maps obtained in the present work show that complete ordering occurs in the case of $TiFe_2$ and $TiMn_2$.

Analysis of table 1 shows that the atomic parameters x and z obtained for the two alloys deviate, beyond the error limits, from the ideal values, $1/6$ and $1/16$ respectively, in these structures.

In the case of $TiFe_2$ the present results agree, within the experimental uncertainty, with those determined by Brückner *et al.* [12]. Their results were obtained by powder neutron diffraction from the observed intensities of 13 reflections and the composition of the specimen used was not stoichiometric. It should be pointed out that a considerably smaller standard deviation for the z -parameter is given in the present work.

The ratio R_A/R_B for the two alloys, $TiFe_2$ and $TiMn_2$, are respectively 1.14 and 1.11₅. Two distinct values were found for the interatomic distance A-A (Ti-Ti), as well as for the B-B distance (Fe-Fe or Mn-Mn), as can be seen in table 2. This has already been pointed

Table 2— Interatomic distances in the Laves phases $TiFe_2$ and $TiMn_2$.

Position	Atom	Neighbours	Distances		Other neighbours
			$TiFe_2$ (AB_2)	$TiMn_2$ (AB_2)	
f	A (Ti)	1 f	2.939	2.950	1 f, 1 f
		1 f	2.907	2.970	
		3 h	2.799	2.844	2 a, 1 a
		6 h	2.783	2.830	
a	B	6 h	2.414	2.442	6 f
h	B	2 h	2.336	2.366	6 f, 2 a 2 f, 2 f, 2 f
Atomic radii (CN12)			Ti	Fe	Mn
			1.45	1.27	1.30

out for other Laves phases when the axial ratio deviates from 1.63. One of the two Ti-Ti interatomic distances only depends on c and z whereas the calculation of the other involves, besides the z -coordinate, both lattice parameters a and c . The z -parameter is the same for both structures, within the experimental error; hence the difference between Ti-Ti distances, which occurs in $TiFe_2$ and in $TiMn_2$, should be attributed to their significantly different lattice parameters a and c .

The calculated contraction of the B-B interatomic distance based on the structure geometry and on the parameters a and c known for a large number of C14 Laves phases decreases with increasing R_A/R_B . When these contractions are plotted against the atomic radii they fall on a band with a well defined slope (Nevitt, [3], fig. 15). If the B-B contraction were determined by geometrical factors only, the mentioned values should fall on a straight line intersecting the horizontal axis at $R_A/R_B = 1.225$.

Plotting, as above, the contractions of the distances Fe-Fe and Mn-Mn calculated from the results shown in table 2, they fall well above that straight line; this indicates an additional contraction of the Fe and Mn atoms, which cannot be attributed to geometrical factors. Furthermore, this contribution is not the same in the two alloys, but appears to decrease with increasing atomic number of the B element (5.1% and 7.8% for the two Fe-Fe distances; 6.1% and 8.8% for the two Mn-Mn distances).

Berry and Raynor [13] suggested that an additional contraction dependent on the position of B in the periodic table, and hence on its electronic configuration, can occur in some Laves phases (AB_2) as a result of an interaction between A and B atoms.

The contractions observed in both $TiFe_2$ and $TiMn_2$ alloys appear to confirm the above assumption; furthermore, they indicate that the contraction associated with the B element decreases with increasing number of 3d electrons. Since cobalt follows manganese and iron along the same transition series the study of the $TiCo_2$ structure would be of great interest.

We would like to thank Prof. S. Garcia-Blanco and Prof. S. Martínez-Carrera of "Instituto de Química-Física Rocasolano, Consejo Superior de Investigaciones Científicas", Madrid, Spain, for the provision of facilities on the automatic diffractometer and processing of the data.

REFERENCES

- [1] SINHA A. K. — *Progress in Materials Science* **15**, 93 (1972).
- [2] LAVES F. and WITTE H. — *Metallwirt.* **15**, 840 (1936).
- [3] NEVITT, M. V. — «*Electronic Structure and Alloy Chemistry of the Transition Elements*» — (ed. P. A. Beck); Interscience; New York (1968).
- [4] PEARSON W. B. — *Acta Cryst.* **B 24**, 7 (1968).
- [5] MURAKAMI Y. and ENJYO T. — *J. Japan Inst. Metals* **22**, 261 (1958).
- [6] MURAKAMI Y., KIMURA H. and NISHIMURA Y. — *Trans. Nat. Res. Inst. Met. Japan* **1**, 7 (1958).
- [7] FARQUAR M. C. M. and LIPSON H. — *Proc. Phys. Soc.* **58**, 200 (1946).
- [8] WALLBAUM H. J. — *Z. Krist.* **A 103**, 391 (1941).
- [9] DUWEZ P. and TAYLOR J. L. — *J. Metals* **2**, 1173 (1950).
- [10] FORSYTH J. B. and WELLS M. — *Acta Cryst.* **12**, 412 (1959).
- [11] DAMJANOVICK A. and BLACK P. J. — *Acta Cryst.* **14**, 987 (1961).
- [12] BRÜCKNER W., KLEINSTÜCK K. and SCHULZE G. E. R. — *Phys. Stat. Sol.* **23**, 475 (1967).
- [13] BERRY R. L. and RAYNOR G. N. — *Acta Cryst.* **6**, 178 (1953).