

The Crystal Structure of ZrFeP and Related Compounds

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The crystal structure of ZrFeP has been determined and refined by single-crystal X-ray diffraction methods. ZrFeP crystallizes with the *anti*-PbCl₂ (*C* 23)-type structure, in which the zirconium and the iron atoms occupy ordered positions. Compounds isostructural with ZrFeP occur in several ternary phosphide, silicide and germanide systems, and their crystal-chemical properties are discussed.

Many ternary systems of the type Me—Fe—P, where Me is a transition metal, have been studied by R. Vogel and coworkers (reported in a series of articles published in *Archiv für Eisenhüttenw.* from 1929 onwards). Vogel's investigations comprise determinations of the equilibrium diagrams by means of thermoanalytical and metallographic methods. The occurrence of several ternary phases has been reported. The crystal structures of these compounds have not been determined, however, and in general the crystal chemistry of the ternary phosphide systems is very incompletely known.

The present investigation concerns the crystal structure of the ternary compound ZrFeP originally discovered by Vogel and Dobbener.¹ In addition, the occurrence of some further ternary phosphides isostructural with ZrFeP is reported.

PREPARATION, X-RAY DIFFRACTION WORK AND NUMERICAL COMPUTATIONS

The alloys were prepared from metals with purities of better than 99.8% and red phosphorus of purity greater than 99%. The ternary phases containing titanium and zirconium were synthesized in the following manner. Monophosphides of iron and cobalt were prepared by heating metal powder and red phosphorus in evacuated and sealed silica tubes. Mixtures of these monophosphides and titanium or zirconium metal were then melted in an argon-arc furnace. The other ternary phosphides were synthesized by heating mixtures of the component elements in evacuated silica tubes, followed by an arc-melting of the products.

The alloys were investigated by powder diffraction methods employing Guinier-Hägg focussing cameras and CrK_α-radiation. Silicon ($a = 5.43054 \text{ \AA}$) was used as the internal calibration standard. The single-crystal X-ray examination was made with a Weissenberg camera using zirconium-filtered MoK-radiation. The reflexions were recorded using the multiple-film technique with thin iron foils interleaved between successive films, and the intensities were estimated visually by comparison with a calibrated intensity scale.

Numerical computations were made on a CDC 3600 computer employing programs according to the following list:

Least-squares refinement of unit cell dimensions	J. Tegenfeldt, Uppsala
Lorentz-polarisation factor corrections, structure factor calculations, Fourier summations	A. Zalkin, Berkeley; modified by R. Liminga and J. O. Lundgren, Uppsala
Least-squares refinement of positional parameters and temperature factors	P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles; modified by A. Zalkin, Berkeley and by C.-I. Brändén, R. Liminga and J. O. Lundgren, Uppsala
Interatomic distances	A. Zalkin, Berkeley

THE STRUCTURE OF ZrFeP

In their studies of the Zr—Fe—P system, Vogel and Dobbener¹ observed the occurrence of the ternary compound ZrFeP. This phase was stated to melt congruently and to have a very restricted range of homogeneity.

These observations were confirmed in the present work. The ternary compound was easily prepared, and well-developed single-crystals were formed directly when the melts cooled. A preliminary examination using X-ray powder diffraction methods indicated a relatively simple structure. Crystal-chemical considerations (see the discussion below) suggested the *anti*-PbCl₂-type structure as a highly probable atomic arrangement, and an attempt to index the powder pattern on the basis of this hypothesis was immediately successful. There are two crystallographically non-equivalent metal positions in the *anti*-PbCl₂-type structure. It appeared probable that each of these positions should be occupied by only one kind of metal atom in the ternary phosphide. In order to investigate this possibility more closely it was decided to make a complete single-crystal determination of the structure.

The results of the single-crystal studies were in complete accord with the structure proposed. There were no indications of a symmetry lower than *Pnma*, and therefore the intensities of the *h0l* reflexions only were used for the structure refinement.

The *anti*-PbCl₂-type structure has been studied previously in some detail by one of the present authors,^{2,3} and the notations Me_I and Me_{II} for the two non-equivalent metal atom positions used earlier are retained in the present paper. It seemed probable that the zirconium atoms should occupy the Me_{II} positions and the iron atoms the Me_I positions, and a preliminary calculation of the electron density projection $\rho(x,z)$ supported this idea. The subsequent structure refinement was therefore based on this distribution of the zirconium and iron atoms.

The refinement was made by the least-squares method. Only observed reflexions were included, and the weights assigned were according to the formula $w = 1/(a + |F_o| + c|F_o|^2)$ following a suggestion by Cruickshank.⁴ The final values for the constants were $a = 4.10$ and $c = 0.134$. Atomic scattering factors, including dispersion corrections, were taken from Ref. 5. The crystal selected for the structure determination had a rather uniform cross-section of about 0.05 mm and the absorption correction was neglected. The

refinement converged satisfactorily, and the final R -value for the 111 observed $h0l$ reflexions was 0.089. The extinction effects appeared to be quite small. A final difference synthesis did not contain any significant maxima or minima, and the isotropic temperature factors returned by the least-squares program appeared to have normal values. These observations indicate that the initial assumption about the ordered distribution of the zirconium and iron atoms is valid to a high degree of accuracy.

The final structure data for ZrFeP are as follows:

ZrFeP						
Space group $Pnma$ $Z = 4$.						
$a = 6.3088 \pm 0.0004$ Å; $b = 3.7401 \pm 0.0002$ Å; $c = 7.1717 \pm 0.0004$ Å.						
	x	$\sigma(x)$	z	$\sigma(z)$	B (Å ²)	$\sigma(B)$
4 Zr in 4 c	0.0199	0.0004	0.1830	0.0003	0.16	0.03
4 Fe in 4 c	0.1468	0.0006	0.5615	0.0005	0.25	0.04
4 P in 4 c	0.7782	0.0012	0.6160	0.0009	0.32	0.08

The interatomic distances and their standard deviations are given in Table 1. A list of observed and calculated structure factors can be obtained from this Institute on request.

Table 1. Interatomic distances and their standard deviations (Å units) in ZrFeP. Distances shorter than 4 Å listed.

	Dist.	S.d.		Dist.	S.d.
Zr — 2 P	2.683	0.005	P — 2 Fe	2.311	0.004
— 1 P	2.693	0.007	— 1 Fe	2.358	0.008
— 2 P	2.695	0.006	— 1 Fe	2.457	0.007
— 2 Fe	2.821	0.003	— 2 Zr	2.683	0.005
— 1 Fe	2.830	0.004	— 1 Zr	2.693	0.007
— 1 Fe	2.935	0.004	— 2 Zr	2.695	0.006
— 2 Fe	2.946	0.003	— 1 Zr	3.459	0.007
— 2 Zr	3.233	0.004	— 2 P	3.694	0.007
— 2 Zr	3.297	0.001	— 2 P	3.740	0.000
— 1 P	3.459	0.007	— 2 P	3.754	0.013
— 2 Zr	3.740	0.000			
Fe — 2 P	2.311	0.004			
— 1 P	2.358	0.008			
— 1 P	2.457	0.007			
— 2 Fe	2.776	0.005			
— 2 Zr	2.821	0.003			
— 1 Zr	2.830	0.004			
— 1 Zr	2.935	0.004			
— 2 Zr	2.946	0.003			
— 2 Fe	3.740	0.000			

DISCUSSION

In a previous discussion of the *anti*-PbCl₂-type structure³ it was mentioned that the compounds crystallizing with this structure can be divided into two sub-classes with respect to their atomic coordination. (It is also possible to distinguish a third sub-class with Re₂P as the only known representative).

Typical representatives for the two sub-classes are Co_2Si and Co_2P , respectively, and the coordination in the Co_2P and Co_2Si structures is summarized in Table 2.

Table 2. The atomic coordination in typical representatives for the Co_2Si and Co_2P sub-classes of the *anti*- PbCl_2 -type structure. (N_{Me} = number of near metal neighbours; N_{X} = number of near non-metal neighbours)

	N_{Me}	N_{X}	$N_{\text{Me}} + N_{\text{X}}$
The Co_2Si sub-class			
Me_{I}	8	5	13
Me_{II}	8	5	13
X	10	—	10
The Co_2P sub-class			
Me_{I}	8	4	12
Me_{II}	10	5	15
X	9	—	9

The differences in coordination between the two sub-classes are connected with differences in the positional parameters of the atoms and also with an appreciable difference in the shape of the unit cells. As mentioned in Ref. 3, and also noted by C. B. and D. P. Shoemaker,⁶ the ratio a/c for compounds belonging to the Co_2Si sub-class lies in the range 0.67–0.73, while this ratio ranges between 0.79 and 0.85 for members of the Co_2P sub-class. It might thus be possible to classify an *anti*- PbCl_2 -type compound with respect to its type of coordination merely by determining its a/c ratio without actually making a complete structure determination. It must be stressed, however, that the division between the sub-classes is by no means sharp, and borderline cases may well occur.

It is seen from the values in Table 2 that a structure of the Co_2P sub-class would be particularly suited for ternary compounds containing two kinds of metal atoms with different radii. Following the principle of good space-filling, the larger metal atoms should preferentially occupy the Me_{II} position with the highest coordination number, while the smaller metal atoms should occupy the Me_{I} positions. The non-metal atoms have the coordination number nine, which is particularly common with phosphides and arsenides, and is also frequently found in silicides and germanides.³

It is therefore hardly surprising that a large number of ternary silicides and germanides crystallize with the Co_2P -type structure. These compounds, originally denoted by *E*-phases by Westbrook, DiCerbo and Peat,⁷ contain transition metal atoms from groups IV and V as the larger atoms and iron group metal atoms as the smaller atoms. The occurrence of more than twenty *E*-phases has been reported by Spiegel, Bardos and Beck.⁸ An accurate single-crystal structure determination of TiNiSi was recently made by C. B. and D. P. Shoemaker,⁶ and the result is completely analogous with that obtained for ZrFeP .

An exploratory survey of some ternary $\text{Me}'\text{—Me}''\text{—P}$ systems yielded the Co_2P -type phases listed in Table 3. The occurrence of TiFeP has been reported earlier by Vogel and Giessen,⁹ while the remaining compounds have not been characterized previously.

Table 3. Unit cell dimensions for some ternary Co₂P-type phosphides.

Compound	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>U</i> (Å ³)	<i>a/c</i>
TiFeP	6.007	3.602	6.897	149.2	0.871
TiCoP	6.036	3.556	6.872	147.5	0.878
ZrFeP	6.309	3.740	7.172	169.2	0.880
ZrCoP	6.332	3.698	7.160	167.7	0.884
NbFeP	6.139	3.585	7.006	154.2	0.876
NbCoP	6.112	3.587	6.978	153.0	0.876
NbNiP	6.108	3.578	7.091	155.0	0.861
TaFeP	6.099	3.574	6.976	152.1	0.874
TaCoP	6.077	3.573	6.961	151.1	0.873
TaNiP	6.058	3.566	7.046	152.2	0.860

No detailed analyses of the phase-relationships were made, but in some of the systems extended homogeneity ranges of the Co₂P-type phases were indicated. Deviations from the ideal composition may occur through Me'—Me'' substitution as well as through the formation of vacancies in the metal lattice as observed² for the binary phosphide Co₂P. Furthermore, the unit cell dimensions may exhibit variations even if the composition of the alloy is unchanged, depending on the degree to which the Me' and Me'' atoms take ordered positions on the two non-equivalent metal atom sites in the structure.

The values quoted in Table 3 should therefore mainly be taken as proof for the occurrence of Co₂P-type phases in the various systems, while the actual numerical values for the unit cell dimensions, although determined to a high degree of accuracy in each instance, should be regarded with some caution. The *a/c* values for the compounds listed in Table 3 all lie between 0.86 and 0.89.

The list of *E*-phases in ternary phosphide systems as given in Table 3 is certainly not complete. There are also strong reasons for believing that a further number of isostructural compounds containing arsenic can be prepared. In analogy to, *e.g.*, the Laves phases, the abundance of *E*-phases is most probably due to the particularly favourable geometrical properties of the structure, allowing atoms of different sizes to be neatly accommodated within a comparatively small unit cell.

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