

The Crystal Structure of FeAs

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The crystal structure of FeAs has been determined from three-dimensional, single crystal X-ray data. The structure is essentially of the MnP type, but the deduced space group $Pna2_1$ lacks a mirror plane compared with that currently assumed for the structure of MnP. The least squares refined Guinier photographic data gave the following unit cell dimensions and standard deviations: $a=5.4420 \pm 0.0007$ Å, $b=6.0278 \pm 0.0007$ Å, $c=3.3727 \pm 0.0006$ Å. The unit cell contains 4 Fe and 4 As atoms in position 4(a) with $x=0.0027 \pm 0.0005$, $y=0.1994 \pm 0.0005$, $z=1/4$ for Fe and $x=0.1992 \pm 0.0004$, $y=0.5773 \pm 0.0004$, $z=0.264 \pm 0.003$ for As. (The error limits equal the standard deviations obtained from the least squares refinements.) The Fe atoms show anisotropic thermal motion, whereas isotropic temperature factors were found for the As atoms.

A review article by Kjekshus and Pearson¹ lists some 30 binary compounds with the MnP type crystal structure. With one technical exception (AuGa), all of these compounds contain a transition element in combination with a metalloid component from the groups IVB to VIB of the Periodic System.

The structural arrangement in MnP corresponds to a somewhat distorted form of that in NiAs, the latter structure type and/or closely related variants thereof being found in numerous similar transition metal systems. Despite the close structural resemblance of the MnP and NiAs types, and the generally close correspondence of the atomic components, the physical and chemical properties of the phases belonging to the two categories are normally quite different. The most notable difference is that the phases with the NiAs type structure frequently exhibit broad (temperature dependent) ranges of homogeneity, which often exclude the equiatomic composition, whereas those with the MnP type structure generally appear to exist only with the 1:1 stoichiometric ratio (with the possible exceptions of those modifications of "TiSe"² and "VS"^{3,4} which have the MnP type structure). A detailed study of the compounds with the MnP type structure may, apart from its own merits, be of considerable interest in relation to the light which may possibly be thrown on phases with the NiAs type structure. A research programme is accordingly being undertaken at this Institute in order to establish the properties of a number of compounds with the MnP type structure.

The present article concerns a critical redetermination of the crystal structure of FeAs, the atomic parameters of which have hitherto been available with only an inadequate accuracy. Hägg⁵ was the first to note that FeAs crystallizes orthorhombically, and that its structure is only related to, rather than isostructural with, that of NiAs. The structure of the prototype MnP was solved by Fylking⁶ (on the basis of single crystal and powder X-ray data), who furthermore showed that FeP, CoP, MnAs, FeAs, and CoAs are isostructural compounds.

Although the MnP type structure is nowadays regarded as well established, the atomic parameters for the various compounds belonging to this class have not generally been determined with an accuracy corresponding to its simplicity. The most accurate structure determinations have been carried out^{7,8} for MnP, FeP, CoP, and MnAs, the atomic parameters for most of the other compounds are given to the second or third decimal place (*cf.* Pearson⁹), and in a few cases only the unit cell dimensions are known. An important objection to all the previous work on these structures is that the highest symmetric space group according to the systematic extinctions (*Pnma* or its equivalents) has been accepted without being properly verified. An alternative space group, which would generate very nearly the same atomic arrangement, is indeed possible, and one of the aims of the present study was to choose between these possibilities in the case of FeAs.

EXPERIMENTAL

The samples were prepared from 99.99 + % Fe (Johnson, Matthey & Co., Ltd.; turnings from rods) and 99.999 + % As (Fluka AG) by heating weighed quantities of the components in evacuated and sealed silica tubes at 850°C for 10 days. After careful grinding, the samples were annealed at 850°C for another 10 days and finally cooled to room temperature over a period of 3 days. Several samples with different initial compositions were prepared, on both sides of the 1:1 stoichiometric ratio. A considerable number of FeAs single crystals were found in the capsules after the heat treatment.

X-Ray powder photographs of all samples were taken in a Guinier type camera of 80 mm diameter with monochromatized $\text{CuK}\alpha_1$ -radiation ($\lambda = 1.54050 \text{ \AA}$) using KCl ($a = 6.2919 \text{ \AA}$ ¹⁰) as internal standard. The lattice dimensions were refined by applying the method of least squares to the diffraction data.

Single crystal X-ray photographs were taken in an integrating Weissenberg camera of 57.3 mm diameter with $\text{MoK}\alpha$ -radiation using the multiple-film technique. Three-dimensional data of, in all, 410 reflections (130 with zero intensity) were collected from the layers $hk0$ to $hk2$ and $h0l$ to $h4l$. The intensity measurements were carried out microphotometrically except for the weakest reflections which were estimated visually. An approximately spherical crystal of $\sim 0.12 \text{ mm}$ diameter was used to obtain the intensity data. The intensities were corrected for the combined Lorentz and polarization factors, and for absorption ($\mu R = 2.7$) and secondary extinction.

The atomic scattering factors for the calculations of F_c -values were taken from Hanson *et al.*¹¹ The least squares refinements were carried out according to the programme of Gantzel *et al.*¹² The degree of agreement between the observed and calculated structure factor data is judged from the average and weighted reliability factors

$$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$R^* = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{\frac{1}{2}}$$

where w denotes the weight factor. The unobserved reflections are not included in the calculations of R and R^* and furthermore are omitted from the least squares refinements. (The observed and calculated structure factor data are available from the authors upon request.)

RESULTS

(i) *Homogeneity range and composition.* The unit cell dimensions (see section ii) of the FeAs phase were found to be invariant within the experimental error limits for samples with different initial compositions. Since a range of homogeneity is in most cases detectable by corresponding changes in the lattice dimensions, it is accordingly concluded that this phase has such a narrow homogeneity range that it must be considered as a compound with well defined composition.

Application of the disappearing phase principle to the Guinier photographs of samples with different initial proportions of Fe and As gave the composition $\text{FeAs}_{1.00 \pm 0.02}$, the uncertainty in the determination being indicated by the limits of error. (The minor phases admixed with FeAs in these samples were found to be Fe_2As and FeAs_2 in accordance with the phase relationship described by Pearson.⁹) The stoichiometric formula FeAs was furthermore confirmed by comparison of the pycnometrically determined density with that calculated from the unit cell dimensions for $\text{FeAs}_{1.00}$ (see section ii).

(ii) *Unit cell and space group.* The Guinier and Weissenberg photographs of FeAs are easily indexed on orthorhombic axes: $a = 5.4420 \pm 0.0007 \text{ \AA}$, $b = 6.0278 \pm 0.0007 \text{ \AA}$, $c = 3.3727 \pm 0.0006 \text{ \AA}$. (The indicated error limits are equal to the standard deviations obtained in the least squares refinements of the Guinier photographic data.) These data agree well with those reported by Fylking⁶ and Heyding and Calvert,¹³ when one appreciates that different settings of the unit cell are being used in the three studies.

The systematic extinctions in the diffraction data are of the type $0kl$ absent when $k+l=2n+1$ and $h0l$ absent when $h=2n+1$. The possible space groups are accordingly limited to $Pna2_1$ and $Pnma$ (b and c interchanged), these conditions also being characteristic of the prototype MnP.^{6,7}

The observed density of 7.804 g cm^{-3} shows that the unit cell contains 4 FeAs-groups ($Z_c = 3.98$).

(iii) *Refinements of the structure.* There was no decisive reason to question the overall correctness of the MnP type structure for FeAs, and least squares refinements could accordingly be started at once. Essentially the same MnP type atomic arrangement is attainable in both possible space groups, and in order to promote a test of the presence or absence of the mirror plane characterizing the space group of higher symmetry, a description based on $Pna2_1$ was chosen for these calculations. In terms of space group $Pna2_1$ the MnP type structure places 4Fe and 4As atoms in position $4(a)$, i.e. x, y, z ; $\bar{x}, \bar{y}, \frac{1}{2} + z$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; $\frac{1}{2} + x, \frac{1}{2} - y, z$ with $x \approx 0.01$, $y \approx 0.19$, $z \approx 1/4$ for Fe and $x \approx 0.20$, $y \approx 0.58$, $z \approx 1/4$ for As; cf. Fylking.⁶ One of the z -parameters can obviously be ascribed an arbitrary fixed value without introducing any reduction in the generality of the final solution. In order to facilitate comparison of the two space groups, the z -parameter of Fe has accordingly been fixed at $1/4$ and kept constant throughout the present calculations.

Including the possibility of anisotropic thermal vibrations of the atoms, there were a number of different models to be tested by the least squares refinements. Some of these alternatives proved afterwards to be uninteresting, and the results presented in Table 1 comprise only the six models which

Table 1. Final positional parameters and temperature factors (in Å²), with associated standard deviations for six possible refinement models for FeAs according to space group *Pna2₁*.

Refined parameters	Restrained models						Unrestrained model	
	$z_{\text{As}} = \frac{1}{4}$, isotr. B_{Fe} and B_{As}	$z_{\text{As}} = \frac{1}{4}$	Isotr. B_{Fe} and B_{As}	Isotr. B_{Fe}	Isotr. B_{As}			
Fe	x	0.0027 ± 0.0005	0.0027 ± 0.0005	0.0027 ± 0.0005	0.0027 ± 0.0005	0.0027 ± 0.0005	0.0027 ± 0.0005	
	y	0.1994 ± 0.0005	0.1994 ± 0.0005	0.1995 ± 0.0005	0.1995 ± 0.0005	0.1994 ± 0.0005	0.1994 ± 0.0005	
	z	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	
	B_x	} 0.36 ± 0.04	0.24 ± 0.06	} 0.33 ± 0.04	} 0.33 ± 0.04	0.22 ± 0.06	0.22 ± 0.06	
	B_y		0.32 ± 0.07			0.32 ± 0.07	0.32 ± 0.07	
B_z	0.60 ± 0.08		0.51 ± 0.08			0.51 ± 0.08		
As	x	0.1993 ± 0.0004	0.1992 ± 0.0004	0.1992 ± 0.0004	0.1992 ± 0.0004	0.1992 ± 0.0004	0.1992 ± 0.0004	
	y	0.5774 ± 0.0004	0.5773 ± 0.0004	0.5773 ± 0.0004	0.5773 ± 0.0004	0.5773 ± 0.0004	0.5773 ± 0.0004	
	z	$\frac{1}{4}$	$\frac{1}{4}$	0.266 ± 0.003	0.266 ± 0.003	0.264 ± 0.003	0.264 ± 0.003	
	B_x	} 0.30 ± 0.03	0.31 ± 0.05	} 0.31 ± 0.03	} 0.28 ± 0.05	} 0.31 ± 0.03	} 0.31 ± 0.05	
	B_y		0.29 ± 0.05					0.29 ± 0.05
B_z	0.31 ± 0.05		0.35 ± 0.05					0.33 ± 0.05
R	0.0936	0.0903	0.0907	0.0902	0.0884	0.0884	0.0884	
R^*	0.1170	0.1141	0.1139	0.1135	0.1122	0.1120	0.1120	
\mathcal{R}	1.045	1.018	1.017	1.013	1.002	—	—	

appeared to have reasonable significance. Referring to the models with anisotropic temperature factors, it should be noted that the first refinement cycles were performed according to the complete, six term, tensor expression for the thermal parameters β_{ij} . However, the calculations showed that the tensor components for the mixed terms ($i \neq j$) were generally almost identical zero and considerably smaller than the corresponding standard deviations, and their values were accordingly fixed at zero in the final calculations. (This result implies that the principle axes of the vibration ellipsoids of the atoms coincide with the crystallographic axes.) The least squares refinement processes for the various models proceeded until insignificant shifts were obtained for all variables, the final reliability factors R and R^* being included in Table 1.

From the values of the parameters listed in Table 1 and their associated standard deviations, it may be concluded that space group $Pna2_1$ gives the most correct description of the crystal structure of FeAs. The parameter z_{As} differs from the special value $1/4$ required by the more symmetric space group by approximately five standard deviations for all models where it has been allowed to vary. Similar considerations for the thermal parameters may suggest that the Fe atoms vibrate anisotropically, whereas the As atoms appear to have isotropic motions. The best set of parameters for FeAs should accordingly be that printed in *Italics* in Table 1.

It is also possible to arrive at the same conclusion in a somewhat different, but statistically more satisfactory way, by applying the significance test proposed by Hamilton.¹⁴ According to Hamilton one may utilize the R^* -factor ratio $\mathcal{R} = R_r^*/R_u^*$ (where R_u^* and R_r^* denote the weighted reliability factors resulting from refinements of unrestrained and restrained models, respectively) to judge the relative probability of the correctness of the various models. The value of \mathcal{R} (*cf.* Table 1) together with the dimension of the hypothesis and the degrees of freedom of the data have been used to estimate the significance levels of the different models from the tabulated data for significance points of \mathcal{R} given by Hamilton. According to this scheme, the hypothesis that FeAs crystallizes in space group $Pnma$ can be rejected at a significance level better than 0.005 regardless of whether the temperature factors are isotropic or anisotropic. Considering the question of isotropy of temperature factors for models involving space group $Pna2_1$, application of the Hamilton test shows that the model with anisotropic motions of both Fe and As has no statistical preference (significance level >0.50) over the model which assumes isotropic vibrations for As. The model with an isotropic temperature factor for Fe only can, on the other hand, be rejected at an interpolated significance level of 0.04, whereas that with isotropic temperature factors for both kinds of atoms leads to rejection at an interpolated significance level of 0.07. The final conclusion reached by application of the Hamilton test is accordingly that the most correct parameter set for FeAs is that printed in *Italics* in Table 1 (*vide supra*). It is relevant to emphasize that this conclusion refers to the conditions at room temperature, since the deviation of z_{As} from $1/4$ may be expected to increase at lower temperatures where the temperature factors as well as their inherent anisotropy will finally become negligible.

(iv) *Interatomic distances and angles.* Some important interatomic distances and angles calculated from the unit cell dimensions and the best parameter

set in Table 1 are listed in Table 2. In the structure (Fig. 1) each Fe atom is octahedrally coordinated to six near As atoms and each As atom is surrounded by six near Fe atoms in a trigonal prismatic configuration. Both kinds of coordination polyhedra are far from being of regular shapes; *cf.* Table 2.

The reduction in the symmetry of the coordination polyhedra introduced by the presently revised data constitutes only a minor part of their total irregularities. The lack of the mirror plane in space group $Pna2_1$ leads to complete non-equivalence of all the interatomic Fe—As distances (Table 2).

Table 2. Some important interatomic distances and angles in the crystal structure of FeAs. (Indicated error limits are calculated from the standard deviations in axes and parameters.)

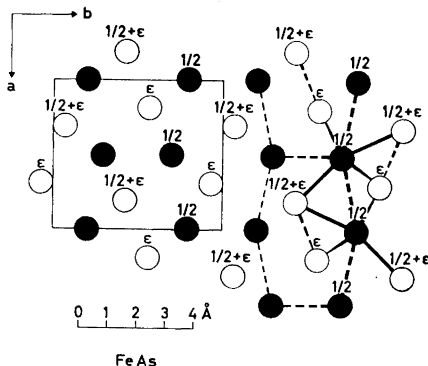
Interatomic distances (Å)

Type		FeAs
Bonding interatomic distances	Fe—As (1)	2.348 ± 0.004
	Fe—As (1)	2.388 ± 0.007
	Fe—As (1)	2.420 ± 0.007
	Fe—As (1)	2.455 ± 0.007
	Fe—As (1)	2.486 ± 0.007
	Fe—As (1)	2.517 ± 0.004
Possible bonding interatomic distances	Fe—Fe (2)	2.789 ± 0.004
	Fe—Fe (2)	2.937 ± 0.004
	As—As (2)	2.900 ± 0.008
Shortest interatomic distances neglected as bonding	Fe—As	3.900 ± 0.004
	Fe—Fe	3.373 ± 0.001
	As—As	3.373 ± 0.001

Interatomic angles (°)

Type	FeAs	Type	FeAs
As—Fe—As (1)	71.36 ± 0.18	Fe—As—Fe (1)	69.85 ± 0.12
As—Fe—As (1)	72.45 ± 0.18	Fe—As—Fe (1)	70.89 ± 0.22
As—Fe—As (1)	86.84 ± 0.23	Fe—As—Fe (1)	74.75 ± 0.16
As—Fe—As (1)	87.79 ± 0.20	Fe—As—Fe (1)	76.02 ± 0.15
As—Fe—As (1)	88.26 ± 0.23	Fe—As—Fe (1)	86.84 ± 0.10
As—Fe—As (1)	88.70 ± 0.17	Fe—As—Fe (1)	88.27 ± 0.11
As—Fe—As (1)	90.20 ± 0.17	Fe—As—Fe (1)	107.01 ± 0.22
As—Fe—As (1)	90.89 ± 0.21	Fe—As—Fe (1)	109.14 ± 0.22
As—Fe—As (1)	93.45 ± 0.18	Fe—Fe—Fe (1)	70.10 ± 0.09
As—Fe—As (1)	95.21 ± 0.18	Fe—Fe—Fe (2)	99.75 ± 0.11
As—Fe—As (1)	103.55 ± 0.19	Fe—Fe—Fe (2)	100.89 ± 0.11
As—Fe—As (1)	105.63 ± 0.19	Fe—Fe—Fe (1)	154.73 ± 0.15
Fe—As—Fe (1)	68.70 ± 0.21	As—As—As (1)	71.10 ± 0.21

Fig. 1. The crystal structure of FeAs projected along [001]. The filled and open circles represent the iron and arsenic atoms, respectively. The heavy solid lines denote the chemical bonds within the distorted FeAs₄ octahedra and the broken lines indicate the locations of possible bonding interatomic distances. The numbers are fractions of the projection axis, the origin of the diagram being shifted to 0,0,1/4 compared with the text and Table 1 ($\epsilon=0.014$).



Application of the significance test for interatomic distances suggested by Cruickshank^{15,16} shows that the differences between all Fe—As distances are in the highly significant category.

In addition to the definite interatomic Fe—As bonding distances, there also occur some relatively short Fe—Fe and As—As distances (Table 2) which cannot safely be regarded as definitely non-bonding distances. The suggestion of bonding interaction between the Fe atoms appears to be quite probable since these short Fe—Fe distances approach the corresponding values in pure iron (2.48—2.58 Å, depending on the modification of the metal; cf. Pearson⁹). This is supported by the fact that the bonding metal-metal distances in compounds of this type normally exceed their values in the corresponding metals and furthermore exhibit appreciable variation from one crystal structure to another. However, the bonding interatomic distances between non-metal atoms are generally fairly constant. The interpretation of an interatomic As—As distance of 2.900 Å (see Table 2) as bonding is therefore somewhat more doubtful since this value is considerably larger than the expectation value of 2.48 ± 0.08 Å for single As—As bonds.¹⁷

Further experiments are necessary in order to verify the physical reality of these possible bonding interatomic Fe—Fe and As—As distances. However, this ambiguity together with the low symmetry of the coordination polyhedra and the wide range of bonding interatomic Fe—As distances, suggest that the chemical bonding scheme for FeAs may be quite complicated.

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