# Redetermined Crystal Structure of FeAs

KARI SELTE and ARNE KJEKSHUS

*Kjemisk Institutt, Universitetet i Oslo, Blindern, Oslo 3, Norway*

The crystal structures of MnP and its iso-structural compounds are commonly regarded (*cf.*, *e.g.*, Ref. 1) as belonging to space group *Pnma*. However, recent results [2-5] obtained at this institute suggest that the mirror plane perpendicular to [010] is lacking in the crystal structures of some members (*viz.* VAs, FeP, FeAs, and CoAs) of this class. As is frequently the case in science, the basis for an inference of this type is of fundamental importance. In fact, the significance of this simple fact increases the finer distinctions of the object one is examining. The inherent approximations and other limiting conditions concerning our structure determinations of VAs, FeP, FeAs, and CoAs were perhaps not emphasized strongly enough in Refs. 2 − 5. It may therefore be appropriate to reca-pitulate that the latter studies were based on *inter alia* the following limitations:

(i) The photographic (Weissenberg) technique was used to record the diffrac-tion intensities, which in turn were evalu-ated microphotometrically (or visually in the case of the weakest reflections).

(ii) The complex polyhedral shapes of the crystals were approximated to spherical in relation to the corrections for absorption and secondary extinction.

(iii) The effect of dispersion in the scattered X-rays was not taken into ac-count.

The above deficiencies clearly obscure our previous suggestions concerning the space group of VAs, FeP, FeAs, and CoAs, and since specific improvements in these and other respects are now conceivable, it was considered worthwhile to reexamine one of the structures very thoroughly. The structure of FeAs was arbitrarily selected for this purpose. A parallel study has been carried out on a corresponding problem regarding marcasite (FeS$_2$).[6]

*Experimental.* A single crystal of FeAs (from the same batch as that of the preceding study [2]) was ground into an almost perfect sphere of 0.32 mm diameter.

Three dimensional intensity data were re-corded on a computer controlled four-circle

(Syntex) diffractometer using graphite crystal monochromatized MoKα-radiation. The $2\theta{:}\theta$ scan technique was utilized at a variable scan speed, very weak reflections (*viz.* those with intensities less than twice their estimated standard deviations according to counting statistics) being automatically omitted. In all 817 reflections with sin $\theta/\lambda < 1.0$ and indices of the types $hkl$ and $hk\bar{l}$ (according to $Pna2_1$) were registered, and the intensities of 3 check reflections were measured for every 50th reflec-tion during the data collection.

The computational work followed largely the same scheme as in the preceding study.[2] Noteworthy distinctions concern the use of the atomic scattering factors of Doyle and Turner,[7] the inclusion of the real and imaginary parts of the dispersion,[8] and the separate treat-ment of reflections which may be Friedel non-equivalent according to space group $Pna2_1$.

*Results.* A survey of various experi-mental and computational sources of error and other questions which enter into a study of this kind, is given by Brostigen *et al.*[6] and will not be repeated here. Essentially the same refinement models as those used earlier [2-5] were considered, in-cluding anisotropic temperature factors ac-cording to the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. In ad-dition to the specific improvements con-cerning data collection, absorption correc-tion, and dispersion factors (*vide supra*) the effect of omitting low angle reflections from the refinement procedure was examined.

Comparison of the results with different sin $\theta/\lambda$ cuts show that the omission of low angle data has no significant consequence for the refined parameters and the relative values of $R^*$. The results presented in Table 1 refer to a data set with sin $\theta/\lambda > 0.6$. Moreover, only the results obtained for the most unrestrained models according to the space groups $Pnam$ and $Pna2_1$ are in-cluded in the table.

In the case of the models based on space group $Pnam$, all parameters subject to refinement are virtually unaffected by the neglect to take account of dispersion, whereas $R^*$ varies appreciably. The oppo-site situation is seen on comparison of the two models specified in terms of space group $Pna2_1$, where, in particular, the parameters $\beta_{13}$ and $\beta_{23}$ which determine the orientation of the vibrational ellipsoids relative to the crystallographic axes, are affected on the inclusion of dispersion factors.

*Table 1.* Positional parameters and temperature factors with standard deviations for four refinement models of FeAs. (No. of observations, $n = 627$ with sin $\theta/\lambda > 0.60$; only the results for $\Delta f'' > 0$ being presented.)

| Refined parameters | | *Pnam* | | $Pna2_1$ | |
| --- | --- | --- | --- | --- | --- |
| | | Incl. disp. | Excl. disp. | Incl. disp. | Excl. disp. |
| Fe | $x$ | 0.00331(6) | 0.00330(6) | 0.00331(6) | 0.00330(6) |
| | $y$ | 0.19919(5) | 0.19918(6) | 0.19918(5) | 0.19921(6) |
| | $\beta_{11}$ | 0.00192(8) | 0.00144(8) | 0.00199(8) | 0.00149(8) |
| | $\beta_{22}$ | 0.00227(7) | 0.00188(7) | 0.00228(6) | 0.00195(6) |
| | $\beta_{33}$ | 0.0146(2) | 0.0134(2) | 0.0149(2) | 0.0138(2) |
| | $\beta_{12}$ | 0.0000(1) | 0.0000(1) | 0.0001(1) | 0.0000(1) |
| | $\beta_{13}$ | – | – | $-0.0052(7)$ | 0.0001(1) |
| | $\beta_{23}$ | – | – | 0.0026(7) | 0.0026(7) |
| As | $x$ | 0.19915(4) | 0.19914(5) | 0.19914(4) | 0.19912(4) |
| | $y$ | 0.57734(4) | 0.57734(4) | 0.57734(4) | 0.57734(4) |
| | $z$ | $\frac{1}{4}$ | $\frac{1}{4}$ | 0.2510(6) | 0.2519(6) |
| | $\beta_{11}$ | 0.00256(7) | 0.00233(7) | 0.00261(7) | 0.00251(8) |
| | $\beta_{22}$ | 0.00236(6) | 0.00217(6) | 0.00238(6) | 0.00222(6) |
| | $\beta_{33}$ | 0.0087(2) | 0.0080(2) | 0.0088(2) | 0.0085(2) |
| | $\beta_{12}$ | 0.0005(1) | 0.0005(1) | 0.0005(1) | 0.0005(1) |
| | $\beta_{13}$ | – | – | 0.0016(6) | 0.0054(5) |
| | $\beta_{23}$ | – | – | 0.0013(7) | 0.0029(5) |
| $R^*$ | | 0.0301 | 0.0313 | 0.0292 | 0.0293 |
| $\sum w\Delta^2$ | | 2382 | 2575 | 2252 | 2263 |

If judgements were based exclusively on the Hamilton [9] test, the unambiguous conclusion of the present study would be that the crystal structure of FeAs belongs to space group $Pna2_1$ (*cf.* Ref. 2). However, comparison of the difference $(z_{As} - \frac{1}{4})$ with the standard deviation in $z_{As}$, strongly suggests the opposite conclusion. Furthermore, the latter inference is supported by the approximately equal (within the experimental error limits) values found for structure factors which should have been Friedel non-equivalent according to space group $Pna2_1$. The possible deviation of $z_{As}$ from $\frac{1}{4}$ is, in any case, so small that no practical significance is attached to it. The principal cause of the difference between the present and preceding [2] study appears to be associated with the absorption corrections.

In view of the present result we are forced to suspect that our structure determinations of the isostructural compounds CoAs,[3] FeP,[4] and VAs [5] are burdened with corresponding inaccuracies and that they, at least for the time being, should be described in terms of space group *Pnam*. On the other hand, as clearly demonstrated by the comparison of the present and previous results for FeAs, the

$x$ and $y$ parameters for the metal and non-metal atoms of the above structure determinations can be regarded as correct within the error limits stated.

1. Pearson, W. B. *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Pergamon, Oxford — London — Edinburgh — New York — Toronto — Paris — Braunschweig 1967, Vol. II.
2. Selte, K. and Kjekshus, A. *Acta Chem. Scand.* **23** (1969) 2047.
3. Selte, K. and Kjekshus, A. *Acta Chem. Scand.* **25** (1971) 3277.
4. Selte, K. and Kjekshus, A. *Acta Chem. Scand.* **26** (1972) 1276.
5. Selte, K., Kjekshus, A. and Andresen, A. F. *Acta Chem. Scand.* **26** (1972) 4057.
6. Brostigen, G., Kjekshus, A. and Rømming, C. *Acta Chem. Scand. In press.*
7. Doyle, P. A. and Turner, P. S. *Acta Cryst.* **A 24** (1968) 390.
8. Cromer, D. T. *Acta Cryst.* **18** (1965) 17.
9. Hamilton, W. C. *Acta Cryst.* **18** (1965) 502.