structure factors can be calculated directly without any further input of data.

CRAD. The monitor routine controls the input of the programmes from magnetic tape. A register block with information about all programmes, such as programme number and location in core and on tape, is inserted after each programme to reduce search time. When a programme has been executed control is transferred to the monitor specifying the number of the next programme to be read. This can also easily be performed manually from the console. The monitor also contains parts for quickly dumping on to magnetic tape and restoring the content of the core memory.

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The Crystal Structure of Mo_3P

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On the basis of X-ray powder diffraction data Faller *et al.*[1] and Schönberg [2] reported that Mo_3P crystallizes with the Fe_3P-type structure. This result was recently questioned by Rundqvist and Lundström,[3] who pointed out that the structural evidence presented is not conclusive. In particular, the possibility that Mo_3P is isostructural with α-V_3S rather than with Fe_3P can hardly be ruled out by powder diffraction methods alone.

A single-crystal examination of Mo_3P has now been made. The results given below show that the Mo_3P structure does in fact belong to the α-V_3S type.

Polycrystalline samples of Mo_3P were prepared as described previously.[3] It was possible to arc-melt these samples without excessive loss of phosphorus, and needle-shaped Mo_3P crystals were formed directly from the melts, presumably through a peritectic reaction. This observation is not in agreement with the results of Vogel and Horstmann,[4] who reported the occurrence of an Mo—MoP eutectic. This eutectic may possibly be formed under metastable conditions.

Single-crystal diffraction data for Mo_3P were recorded in a Weissenberg camera with zirconium-filtered MoK radiation. The multiple film technique was used with thin iron foils interleaved between successive films, and the intensities were estimated visually. Numerical computations were made on the electronic computers BESK, FACIT EDB, and IBM 7090. In the calculations of structure factors, atomic scattering factors, including the real part of the dispersion correction, were interpolated from the values listed in Ref. 5. The unit cell dimensions were taken from Ref. 3.

The body-centred tetragonal symmetry reported earlier for Mo_3P was confirmed by the single-crystal data. It was further observed that the Laue symmetry is $4/mmm$ which immediately rules out the possibility that Mo_3P has the Fe_3P-type structure (Laue symmetry $4/m$).

At this stage of the structure analysis it appeared reasonable to assume that Mo_3P is iso-structural with α-V_3S. According to Pedersen and Grønvold,[6] the α-V_3S structure is based on space group $I\bar{4}2m$ with two sets of eight vanadium atoms in 8 i positions, eight vanadium atoms in 8 f and eight sulphur atoms in 8 g.

As a preliminary test of the validity of the structure proposal for Mo_3P, an electron density projection on (001) was calculated assuming the x parameters of corresponding atoms to be the same in Mo_3P and α-V_3S. The resulting electron density map contained maxima with the expected positions and heights. After

Table 1. Final structure data for Mo_3P.

Space group $I\bar{4}2m$; $Z = 8$; $a = 9.794$ Å, $c = 4.827$ Å.

		x	$\sigma(x)$	z	$\sigma(z)$	B	$\sigma(B)$
Mo_I	in 8 *i*	0.0926	0.0002	0.7665	0.0008	0.31	0.03
Mo_{II}	in 8 *i*	0.2015	0.0002	0.2660	0.0008	0.28	0.03
Mo_{III}	in 8 *f*	0.3550	0.0003	—	—	0.28	0.03
P	in 8 *g*	0.2911	0.0008	—	—	0.38	0.07

some cycles of refinement with the least squares method good agreement was obtained between observed and calculated *hk*0 structure factors, with the exception of a few strong, low-angle reflexions, which were apparently weakened on account of extinction effects. (These reflexions were excluded in the final refinement.)

The 8 *g* and 8 *f* positions in space group $I\bar{4}2m$ have fixed z coordinates ($\frac{1}{4}$ and 0, respectively), while the 8 *i* position has a free z parameter. In the α-V_3S structure, the two 8 *i* sets of atoms have z parameters close to 0.25 och 0.75, which implies that the intensity sequence in the corresponding *hkl* and *hkl* + 4 reflexions should be closely similar. A visual comparison of the layer lines *hk*0 with *hk*4 and of *hk*1 with *hk*5 showed that the intensity sequence was in fact very similar in Mo_3P apart from minor deviations.

Since the structure proposal satisfied this test, and the interpretation of the *hk*0 intensity material also appeared to be satisfactory, it was decided to proceed directly to a final least squares refinement. In view of the moderate complexity of the structure, a complete three-dimensional refinement was not considered necessary. Accordingly, only the *hk*4 and *hk*5 intensities were estimated and used together with the *hk*0 material in the refinement. The intensities were not corrected for absorption, since the crystal used was quite small (cross-section about 0.05 mm).

The least squares refinement was made on an IBM 7090 machine using the program ORFLS devised by Busing, Martin and Levy.[7] The parameters varied were six positional parameters, four isotropic temperature factors and three scale factors, one for each of the layer lines *hk*0, *hk*4

Table 2. Interatomic distances (Å) in Mo_3P. (Distances shorter than 4.0 Å are listed).

	Mo_I	Mo_{II}	Mo_{III}	P
Mo_I	2.565 2.894 (2) 3.148 (2)	2.844 2.848 2.851 3.076 (2)	2.949 (2)	2.501 (2)
Mo_{II}	2.844 2.848 2.851 3.076 (2)	2.762 (2)	2.794 (2) 3.182 (2)	2.437 (2) 3.194 (2)
Mo_{III}	2.949 (2)	2.794 (2) 3.182 (2)	2.840 3.140 (4)	2.490 (2) 2.493 (2)
P	2.501 (2)	2.437 (2) 3.194 (2)	2.490 (2) 2.493 (2)	3.768 (4)

and *hk*5. Following a suggestion by Cruickshank *et al.*,[8] a weighting scheme according to the formula $w = 1/(a + |F_o| + c|F_o|^2)$, was employed with the constants $a = 72$ and $c = 0.0083$. The refinement was terminated after four cycles. The largest shifts in the parameters were then three orders of magnitude less than the calculated standard deviations, and the R-value for the observed 150 reflexions was 0.057.

The satisfactory convergence of the least squares refinement is taken as final proof that the initial assumptions concerning the Mo_3P structure are correct.

The final structure data obtained are given in Table 1.

Interatomic distances are listed in Table 2. Tables of observed and calculated structure factors can be obtained from the Institute of Chemistry, Uppsala, on request.

The general arrangement of the atoms in the α-V_3S-type structure has been described and discussed by Pedersen and Grønvold [6] and only some comments are given here.

As pointed out by one of the present authors,[9] there is a close relationship between the four structure types Fe_3P, Ti_3P [ε_1(Fe—P—B)], α-V_3S and β-V_3S. In the two former structure types, the non-metal atoms are surrounded by nine near metal neighbours, while in the two latter types there are only eight metal neighbours about the non-metal atoms. The average P—Mo distance in Mo_3P is 2.48 Å which is 0.02 Å shorter than the sum of the Goldschmidt metal radius for 12-coordination (1.40 Å) and the tetrahedral covalent radius of phosphorus (1.10 Å). The P—Mo distance in Mo_3P may be compared with the average P—Mo distances in Mo_4P_3, MoP, and MoP_2, which are 2.48, 2.45, and 2.49 Å, respectively.[10,3]

The molybdenum atoms in Mo_3P have 11—12 molybdenum neighbours at an average distance of 3.01 Å, which exceeds the Goldschmidt metal diameter by 7 %. One of the Mo—Mo distances (Mo_I—Mo_I) is notably short: 2.56 Å. The two Mo_I atoms have six metal neighbours in common, and following the geometrical reasoning by Frank and Kasper,[11] a very short distance between these atoms is therefore to be expected. The geometrical arrangement is analogous in all four of the structure types, Fe_3P, Ti_3P, α-V_3S, and β-V_3S. Accordingly, one very short metal-metal distance occurs in all of these structures.

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