

Refinement of the Ni₃P StructureSTIG RUNDQVIST, EIVIND HASSLER
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The crystal structure of Ni₃P was originally determined by Aronsson¹. In the course of crystal-chemical investigations of transition metal phosphides by one of the present authors (S.R.) it became desirable to obtain accurate structural data for Ni₃P. Accordingly, a re-determination of the structure was made by single-crystal methods.

Weissenberg photographs were taken using zirconium-filtered MoK radiation with crystals rotated about the *a* and *c* axes. The multiple-film technique, with thin iron foils between successive films, was used. The intensities were estimated visually by comparison with a calibrated scale. The structure was refined from successive electron density maps and from difference maps projected on the *ac* and *ab* planes. Corrections for Lorentz and polarisation factors together with Fourier series summations, structure factor calculations, and calculations of interatomic distances were made on the electron digital computer BESK. Atomic scattering factors were interpolated from tables given for nickel by Thomas and Umeda² and for phosphorus by Tomiie and Stam³. Corrections for absorption were not applied. For the 135 *F*(*h**k*0)-values observed, the final *R*-value of 0.083 was obtained. An overall, isotropic temperature factor with *B* = 0.29 Å² was applied. The corresponding figures for the 78 *F*(*h*0*l*)-values observed were *R* = 0.105, *B* = 0.40 Å². (On account of extinction effects, the seven largest *F*(*h**k*0)-values and the largest *F*(*h*0*l*)-value were omitted in the refinements, and were not included in the *R*-values quoted above. Lists of observed and calculated structure factors can be obtained from this Institute on request.)

Final structure data for Ni₃P are given in Table 1. The unit cell dimensions for Ni₃P were determined from powder photographs recorded in Guinier-type focussing cameras with CuKα and CrKα₁ radiation using silicon (*a* = 5.4305 Å) as the internal calibration standard. The accuracy is estimated to be better than 0.04 %. The standard deviations for the atomic posi-

Table 1. Final structure data for Ni₃P.Space-group *I*4̄ (-*S*₄²). *Z* = 8.
a = 8.954 Å; *c* = 4.386 Å; *U* = 351.6 Å³

Atoms in 8(<i>g</i>)	<i>x</i>	<i>σ</i> (<i>x</i>)	<i>y</i>	<i>σ</i> (<i>y</i>)	<i>z</i>	<i>σ</i> (<i>z</i>)
Ni _I	0.0775	0.0003	0.1117	0.0003	0.2391	0.0015
Ni _{II}	0.3649	0.0003	0.0321	0.0003	0.9765	0.0015
Ni _{III}	0.1689	0.0003	0.2200	0.0003	0.7524	0.0015
P	0.2862	0.0005	0.0487	0.0005	0.4807	0.0028

tions quoted in Table 1 were calculated using Cruickshank's⁴ equation. Two different sets of *x* and *y* parameters for each atom were obtained, one from the *F*(*h**k*0) and one from the *F*(*h*0*l*) data. The two sets were not significantly different. The parameter values given in Table 1 are weighted averages obtained by giving the parameter values from the centrosymmetric *ρ*(*xy*) projection twice the weight of those from the non-centrosymmetric *ρ*(*xz*) projection.

A comparison of the data in Table 1 with those given by Aronsson¹ shows a satisfactory agreement. The *x* and *y* parameters are in good agreement, but there are slightly larger differences between the corresponding *z* parameters. This is explained by the fact that Aronsson derived the *z* parameters from the positions of the Patterson peaks alone, without subsequent refinements.

Interatomic distances are listed in Table 2.

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Table 2. Interatomic distances in Ni₃P (Å).
(Distances shorter than 3.6 Å listed)

Ni _I — Ni _I	: 2.43 ₅ , 2.71 ₃ (2), 2.86 ₄ (2)
Ni _I — Ni _{II}	: 2.64 ₅ , 2.90 ₆ , 3.39 ₄
Ni _I — Ni _{III}	: 2.48 ₃ , 2.58 ₄ , 2.71 ₃ 2.72 ₆ , 2.81 ₅
Ni _{II} — Ni _{II}	: 2.48 ₇ , 2.65 ₃ (2), 2.97 ₅ (2)
Ni _{II} — Ni _{III}	: 2.51 ₇ , 2.54 ₆ 2.62 ₂ , 3.48 ₇
Ni _{III} — Ni _{III}	: 2.68 ₅ (2)
Ni _I — P	: 2.22 ₁ , 2.28 ₇ , 3.46 ₇
Ni _{II} — P	: 2.29 ₁ , 2.32 ₂ 2.32 ₆ , 2.34 ₁
Ni _{III} — P	: 2.20 ₈ , 2.27 ₉ 2.33 ₅ , 3.59 ₇

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1. Aronsson, B. *Acta Chem. Scand.* **9** (1955) 137.
2. Thomas, L. H. and Umeda, K. *J. Chem. Phys.* **26** (1957) 293.
3. Tomiie, Y. and Stam, C. H. *Acta Cryst.* **11** (1958) 126.
4. Cruickshank, D. W. J. *Ibid.* **2** (1949) 65.

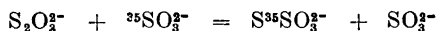
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On the Acceptor Specificity of Rhodanese

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It has previously¹ been shown that rhodanese catalyzes the reaction between thiosulfonates and sulfite to give the corresponding sulfinate and thiosulfate. It could then be expected that rhodanese should also catalyze and exchange reaction between thiosulfate and sulfite



This has now been verified (Table 1), which is of special interest in connection with the experiments on thiosulfate metabolism recently reported by Szczepkowski *et al.*^{2,3} These authors injected ³⁵S-labelled cystine into rats and found that most of the radioactivity was excreted into the urine as sulfate, with only a small fraction as thiosulfate. If, however, unlabelled thiosulfate was injected together with the labelled cystine, much more radioactivity was excreted as thiosulfate and less as sulfate. This was interpreted as indicating that thiosulfate is an important metabolic precursor of sulfate, which is in contrast to current opinions⁴ on the metabolism of sulfur compounds. The most important precursor of sulfate is usually considered to be sulfite, which is formed from cysteine or cystine with cysteinesulfinate as an intermediate. The results of Szczepkowski *et al.* can in fact be explained by a rhodanese catalyzed dilution of labelled sulfite by unlabelled thiosulfate.

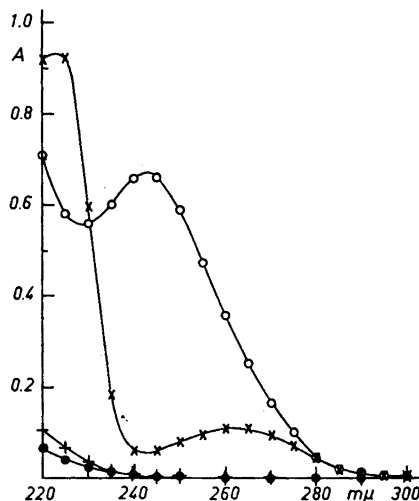


Fig. 1. Absorption spectrum of thiosulfonates and sulfonates. O *p*-toluenethiosulfonate, × *p*-toluenesulfonate, + thioaurine, ● hypotaurine. Each compound at 1×10^{-4} M concentration in 0.05 M phosphate buffer, pH 7.4.

As sulfite is an acceptor for rhodanese, it was of interest to investigate if the structurally related sulfonates (RSO_2^-) could also participate in rhodanese catalyzed transsulfuration reactions. This could be demonstrated to be the case by a spectrophotometric technique, that was based on the fact that arylthiosulfonates (which are very active sulfur donors for rhodanese⁵) show a much stronger light absorption around 240 μ than do the corresponding sulfonates or alkyl thiosulfonates (Fig. 1). It is thus possible to demonstrate a transsulfuration between an aromatic thiosulfonate and an aliphatic sulfinate or between an aliphatic thiosulfonate and an aromatic sulfinate by following the change in light absorption at 240 μ . (Other sulfur acceptors, such as sulfite or cyanide, which absorb weakly at 240 μ , can also be studied in this way). This spectrophotometric technique for following rhodanese catalyzed reactions seems to be of potent value for studies on the reaction mechanism of the enzyme, since it is now possible to rapidly determine what effect different substituents in the donor or acceptor molecule have on the reaction velocity. The rhodanese cata-