Refinement of the Ni$_3$P Structure

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The crystal structure of Ni$_3$P was originally determined by Aronsson. 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 Ni$_3$P. Accordingly, a re-determination of the structure was made by single-crystal methods.

Weissenberg photographs were taken using zirconium-filtered MoK$_\alpha$ 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 Umeda and for phosphorus by Tomio and Stam. Corrections for absorption were not applied. For the 135 $F(hk0)$-values observed, the final $R$-value of 0.083 was obtained. An overall, isotropic temperature factor with $B = 0.29 \text{ Å}^2$ was applied. The corresponding figures for the 78 $F(h0l)$-values observed were $R = 0.105, B = 0.40 \text{ Å}^2$. (On account of extinction effects, the seven largest $F(hk0)$-values and the largest $F(h0l)$-values 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 Ni$_3$P are given in Table 1. The unit cell dimensions for Ni$_3$P were determined from powder photographs recorded in Guinier-type focussing cameras with CuKa$_1$ and CrKa$_1$ radiation using silicon ($\alpha = 5.4305 \text{ Å}$) as the internal calibration standard. The accuracy is estimated to be better than 0.04 %. The standard deviations for the atomic posi-

<table>
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<th>Atoms</th>
<th>$x$</th>
<th>$\sigma(x)$</th>
<th>$y$</th>
<th>$\sigma(y)$</th>
<th>$z$</th>
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<td>0.1117</td>
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<td>0.2300</td>
<td>0.0003</td>
<td>0.7524</td>
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<td>P</td>
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<td>0.0005</td>
<td>0.0487</td>
<td>0.0005</td>
<td>0.4807</td>
<td>0.0028</td>
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</table>

Table 1. Final structure data for Ni$_3$P.

Space-group $I\bar{4}$ ($-S_4^1$), $Z = 8$.

$\alpha = 8.954 \text{ Å}$; $c = 4.386 \text{ Å}$; $U = 351.6 \text{ Å}^3$

The parameters quoted in Table 1 were calculated using Cruickshank's *equation. Two different sets of $x$ and $y$ parameters for each atom were obtained, one from the $F(hk0)$ and one from the $F(h0l)$ 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 $g(xy)$ projection twice the weight of those from the non-centrosymmetric $g(xz)$ projection.

A comparison of the data in Table 1 with those given by Aronsson 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.

Table 2. Interatomic distances in Ni$_3$P (Å).

(Distances shorter than 3.6 Å listed)

<table>
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<tr>
<th>Ni</th>
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<td>2.48, 2.65(2), 2.97(2)</td>
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<tr>
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<td>Ni</td>
<td>2.51, 2.54</td>
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<td>2.62, 3.48</td>
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<td>P</td>
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</tr>
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digital computer BESK were granted by the
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On the Acceptor Specificity
of Rhodanese

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It has previously 1 been shown that
rhodanese catalyzes the reaction between
thiosulfonates and sulfite to give the cor-
responding sulfinate and thiosulfate. It
could then be expected that rhodanese
should also catalyze and exchange reaction
between thiosulfate and sulfite

$$\text{S}_4\text{O}_6^{2-} + \text{HSO}_3^{-} = \text{S}_2\text{O}_3^{2-} + \text{SO}_4^{2-}$$

This has now been verified (Table 1), which is of special interest in connection
with the experiments on thiosulfate me-
bolism 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 ur-
ine as sulfite, 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
sulfite. This was interpreted as indicating
that thiosulfate is an important metabolic
precursor of sulfite, which is in contrast
to current opinions on the metabolism of
sulfur compounds. The most important
precursor of sulfite 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 rho-
danese catalyzed dilution of labelled sulfite
by unlabelled thiosulfate.

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Fig. 1. Absorption spectrum of thiosulfonates
and sulfinites. O p-toluenethiosulfonate, X
p-toluenesulfinate, + thiotaunine, ● hypo-
taurine. Each compound at 1 x 10^{-4} M con-
centration in 0.05 M phosphate buffer, pH 7.4.

As sulfite is an acceptor for rhodanese,
it was of interest to investigate if the struc-
turally related sulfinites (RSO\textsubscript{3}) could
also participate in rhodanese catalyzed
transsulfuration reactions. This could be
demonstrated to be the case by a spectro-
photometric technique, that was based
on the fact that arythiosulfonates (which
are very active sulfur donors for rhoda-

nese 4) show a much stronger light absorp-
tion around 240 \textmu M than do the corre-
sponding sulfinites or alkyl thiosulfonates (Fig.
1). It is thus possible to demonstrate a
transsulfuration between an aromatic tho-

sulfonate and an aliphatic sulfinate or
between an aliphatic thiosulfonate and an
amino sulfinate by following the
change in light absorption at 240 \textmu M.
(Other sulfur acceptors, such as sulfite
or cyanide, which absorb weakly at 240
\textmu M, 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 deter-
mine what effect different substituents
in the donor or acceptor molecule have on
the reaction velocity. The rhodanese cata-