

Crystal Structure Refinements of ZrCoP, NbCoP, NbNiP and TaFeP

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ZrCoP, NbCoP, NbNiP and TaFeP crystallize with the Co_2P (*anti*- PbCl_2)-type structure. The crystal structures have been refined from X-ray single crystal data obtained by visual intensity estimation from Weissenberg films. The special character of the Co–Co interaction in compounds of the type investigated is revealed by the distribution of interatomic distances in the structures.

A large number of ternary transition metal phosphides and arsenides crystallize with the Co_2P -type structure.^{1–7} The chemical and physical properties of these compounds and related phases have been studied extensively (see, for example, Refs. 8–11), and many interesting relationships between properties and atomic arrangement have been observed. ZrFeP has so far been the only ternary phosphide or arsenide for which accurate crystallographic data are available.¹ Detailed structural information on further representatives of this class of compound is thus desirable. In the present paper we report the results from structure refinements of four of the ternary phosphides.

EXPERIMENTAL

Single crystals were obtained from alloys originally prepared by Rundqvist and Nawapong.¹ The crystals selected were almost cylindrical, with the *b* axes directed along the cylinder axes. The crystals were mounted on a Nonius Weissenberg camera with *b* axis as rotation axis. Intensity data were recorded with zirconium-filtered MoK radiation by the multiple-film technique. In the case of NbNiP, light exposed and developed X-ray films

were used as absorbers between successive films in the multiple pack. For ZrCoP, NbCoP and TaFeP, the films were interleaved with thin iron foils. The (*h*0*l*) and (*h*1*l*) zones were recorded for NbNiP, ZrCoP and NbCoP. For TaFeP, only (*h*0*l*) reflexions were recorded. The intensities of the reflexions were measured by visual comparison with intensity scales obtained by timed exposures of one reflexion from each crystal. Absorption corrections were applied to the intensity data by approximating the crystal shape to a cylindrical form.

The crystals were assumed to be isostructural with ZrFeP (space group *Pnma*), and positional parameters and isotropic temperature factors were refined directly by the least-squares method. Atomic scattering factors and corrections for dispersion were taken from the International Tables.¹² Weights were assigned according to Cruickshank's formula,¹³ $w = 1/(c_1 + |F_0| + c_2|F_0|^2)$, where the constants c_1 and c_2 were given appropriate values as judged from weight analyses calculated between successive cycles in the least-squares refinement procedure. The calculations were performed on a CDC 3100 computer using standard crystallographic programs adapted by R. Liminga, University of Uppsala. Unit cell dimensions were taken from the work of Rundqvist and Nawapong, and their standard deviations were assumed to be as reported for ZrFeP.¹

RESULTS AND DISCUSSION

The refinements for all four crystals converged satisfactorily, and the final difference syntheses calculated revealed no significant maxima or minima. The final conventional *R*-values of ZrCoP, NbCoP, NbNiP and TaFeP were 0.06, 0.09, 0.09

and 0.10 for the 153, 114, 224 and 130 observed reflexions, respectively. The structure data obtained are presented in Table 1, where the notations M(1) and M(2) for the two metal positions are the same as those used by Rundqvist and Nawapong: M(1) being occupied by the 3*d* transition metal component, and M(2) by the 4*d* or 5*d* metal component. Due to the approximate character of the absorption corrections, the values for the temperature factors in Table 1 should be regarded with caution, while the positional parameter values can be treated with much greater confidence.

Interatomic distances are given in Table 2. A detailed analysis of these distances provides some information on a curious feature originally pointed out by Rundqvist and Tansuriwongs.² They observed that, for ternary Co₂P-type phases with the general formula M(1)M(2)X (where M(1) is a 3*d* transition metal, M(2) is a 4*d* or 5*d* metal, and X is phosphorus, arsenic, silicon or germanium), compounds with cobalt as the M(1) component invariably have the smallest unit-cell volume for any fixed combination of M(2) and X components. This is somewhat surprising since the normal metal

Table 1. Structure data for ZrCoP, NbCoP, NbNiP and TaFeP. Space group *Pnma* (No 62); all atoms in 4*c* positions, M(1)=Fe, Co, Ni; M(2)=Zr, Nb, Ta. *a*, *b*, *c* in Å; *B* in Å².

	ZrCoP	NbCoP	NbNiP	TaFeP
<i>a</i>	6.332(1)	6.112(1)	6.108(1)	6.099(1)
<i>b</i>	3.698(1)	3.587(1)	3.578(1)	3.574(1)
<i>c</i>	7.160(1)	6.978(1)	7.091(1)	6.976(1)
M(1) <i>x</i>	0.1401(4)	0.1442(10)	0.1471(5)	0.1444(17)
M(1) <i>z</i>	0.5620(4)	0.5609(8)	0.5662(4)	0.5618(13)
M(1) <i>B</i>	0.30(4)	0.15(10)	0.47(4)	0.53(10)
M(2) <i>x</i>	0.0205(3)	0.0249(6)	0.0221(3)	0.0236(4)
M(2) <i>z</i>	0.1833(2)	0.1730(5)	0.1683(3)	0.1751(3)
M(2) <i>B</i>	0.17(3)	-0.12(8)	0.15(2)	0.08(2)
P <i>x</i>	0.2716(8)	0.2764(15)	0.2804(10)	0.269(4)
P <i>z</i>	0.8845(7)	0.8804(16)	0.8765(8)	0.876(3)
P <i>B</i>	0.27(7)	0.07(15)	0.31(7)	0.77(27)

Table 2. Interatomic distances in ZrCoP, NbCoP, NbNiP and TaFeP, (Å). Distances up to 3.5 Å included. M(1)=Fe, Co, Ni; M(2)=Zr, Nb, Ta.

	ZrCoP	NbCoP	NbNiP	TaFeP
M(1)-2P	2.312(4)	2.244(7)	2.282(4)	2.272(16)
-P	2.365(6)	2.285(11)	2.276(7)	2.317(25)
-P	2.455(6)	2.372(12)	2.346(6)	2.333(25)
-2M(1)	2.712(4)	2.655(9)	2.704(5)	2.653(15)
-2M(2)	2.789(2)	2.781(5)	2.794(3)	2.759(7)
-M(2)	2.815(3)	2.804(7)	2.830(4)	2.796(9)
-2M(2)	2.965(3)	2.814(5)	2.795(3)	2.814(8)
-M(2)	2.981(3)	2.842(7)	2.923(4)	2.843(10)
M(2)-2P	2.660(4)	2.598(7)	2.591(5)	2.549(16)
-P	2.666(5)	2.556(11)	2.602(6)	2.568(23)
-2P	2.688(4)	2.605(8)	2.614(5)	2.600(17)
-P	3.473(5)	3.467(11)		3.498(24)
-2M(2)	3.221(2)	3.023(6)	2.995(3)	3.041(3)
-2M(2)	3.307(1)	3.240(2)	3.266(2)	3.224(1)

Table 3. Average near-neighbour distances. M(1)=Fe, Co, Ni; M(2)=Zr, Nb, Ta.

Compound	M(1)–2M(1)	M(1)–6M(2)	M(1)–4P	M(2)–4M(2)	M(2)–5P
ZrFeP	2.776	2.883	2.359	3.265	2.690
ZrCoP	2.712	2.884	2.361	3.264	2.672
NbCoP	2.655	2.806	2.286	3.132	2.592
NbNiP	2.704	2.822	2.297	3.131	2.602
TaFeP	2.653	2.798	2.299	3.133	2.573

radius for nickel is smaller than that of cobalt.

The anomalous unit-cell volume for cobalt-containing crystals is accompanied by a specific distribution of interatomic distances. In order to illustrate this feature more clearly, average near-neighbour distances have been calculated and are given in Table 3, including also distances for ZrFeP.¹ The data in Table 3 reveal that the major difference between NbCoP and NbNiP lies in the Co–Co and Ni–Ni distances. The latter distances exceed the former by more than three times the difference between any other pair of corresponding average distance. An analogous situation occurs for ZrCoP and ZrFeP as regards the Co–Co and Fe–Fe distances; the differences between other distances are here almost insignificant. The singular character of Co–Co metal interactions in ternary phosphides and arsenides of the Co₂P-type, and also the closely related Fe₂P- and Cu₂Sb-types, has been stressed by Fruchart and coworkers (see, for example, Ref. 5). The present results are indeed in good accordance with Fruchart's ideas.

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