The metal-rich part of the Co-Ni-P system at 800 °C

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Abstract: The metal-rich portion of the Co-Ni-P system was studied experimentally at 800 °C by means of evacuated silica glass tube technique. Five binary phases: Co_2P, Ni_2P, $Ni_{12}P_5$, Ni_5P_2, Ni_3P and five ternary phosphides solid solutions: $(Co_{1-x},Ni_x)_3P$, λ_1-$(Ni_{1-x}Co_x)_2P$ (hexagonal), λ_2-$(Co_{1-x}Ni_x)_2P$ (orthorhombic), $(Co_{1-x},Ni_x)_{12}P_5$ and $(Co_{1-x},Ni_x)_5P_2$ were found to be stable in the system. Cobalt has a significant influence on the structure of $(Ni,Co)_2P$ solid solutions and, therefore, cobalt contents might change the crystal structure of naturally occurring phosphides with the Ni/P = 2:1 ratio. Ni-rich, cobalt-containing phosphides with the Ni/P ratio = 3:1 and 2:1, isotypic with minerals schreibersite and barringerite, could possibly be found in meteorites. Likewise, phosphides with Ni/P ratio = 12:5 and 5:2 may possibly be found, but in close association with natural Ni-rich phosphides.

Key-words: phase relations, phosphides, Co, Ni, P.

1. Introduction

Co-Ni phosphides with the metal/phosphorus ratios 3:1 and 2:1 are isotypic with Fe-Ni phosphides known as accessory minerals form differentiated iron-rich meteorites (schreibersite, nickelphosphide, barringerite and allabogdanite). These phosphides usually contain low concentrations of Co (*e.g.* Papike 1998). Co contents in schreibersite range from ~0.14 to 0.39 wt. % Co (Keil, 1968; Leitch & Smith, 1982; El Goresy *et al*., 1988; Ikeda, 1989). An exceptionally high content of 29.3 wt. % Co was reported by Rubin (1984) in schreibersite from the Blithfield meteorite. Also, the Co content in allabogdanite reported by Britvin *et al*. (2002) is low, 1.4 wt. %.

Nevertheless, Co-dominant phosphides have not yet been found in nature, but they could be expected in meteorites anomalously enriched in Co. Cobalt has a remarkable influence on the structure type of Ni (Fe) phosphides with the metal/ phosphorus ratio = 2:1, inducing a transition of the hexagonal structure (Ni-rich) to orthorhombic (Co-rich). It appears that cobalt can change the crystal structure of naturally occurring phosphides.

Nickel and cobalt phosphides have been studied frequently, particularly their magnetic properties (Kubaschewski & Alcock, 1979) and, therefore, phase relations in the binary systems are well known. However, the phase diagram of the ternary Co-Ni-P system is not available in the literature. Therefore, the phase relations in the ternary Co-Ni-P system were studied as a part of a systematic research within the quaternary Co-Fe-Ni-P system.

2. Previous experiments

2.1. Co-Ni system

At 800 °C, cobalt and nickel form a complete cubic ($Fm\overline{3}m$) α-(Co,Ni) solid solution (Nishizawa & Ishida, 1992).

2.2. Co-P system

The phase relations in the system were summarized by Ishida & Nishizawa (1992) and are shown in Fig. 1. One phase, Co_2P, with the *C*23 orthorhombic structure, is stable in the metal-rich portion of the system. There is no phase with the composition Co_3P that would correspond to Ni_3P. Ellner & Mittemeijer (2001) recently distinguished two modifications of Co_2P. According to these authors, at 1154 °C, the low-temperature orthorhombic α-Co_2P converts to the high-temperature β-Co_2P, which melts at 1385 °C. The high temperature β-Co_2P is isotypic with Fe_2P. Crystal structure data of α-Co_2P and β-Co_2P are summarized in Table 1.

2.3. Ni-P system

Phase relations in the metal-rich portion of the system were studied in detail by Lee & Nash (1992) and are shown in Fig. 2. The phases Ni_3P, Ni_5P_2, $Ni_{2.55}P$, $Ni_{12}P_5$, and Ni_2P had previously been described in the literature, of which Lee & Nash (1992) confirmed only Ni_3P, Ni_5P_2, $Ni_{12}P_5$, and Ni_2P as stable. Their crystal structure data are summarized in Table 1.

Table 1. Crystal structure data of metal-rich phosphides in the Co-Ni-P system.

phase	symmetry	space group	lattice parameters			reference
			a	b	c	
α-Co_2P	orthorhombic	$Pnma$	5.6490(3)	3.5126(2)	6.6071(3)	Skála & Drábek (2001)
β-Co_2P	hexagonal	$P\bar{6}2\,m$	5.742(2)	–	3.457(5)	Ellner & Mittemeijer (2001)
Ni_3P	tetragonal	$I\bar{4}$	8.9550(1)	–	4.38737(9)	Skála & Drábek (2000)
Ni_5P_2	hexagonal	$P\bar{3}c$	13.220(2)	–	24.632(2)	Saini *et al.* (1964)
$Ni_{12}P_5$	tetragonal	$I\,4/m$	8.646	–	5.070	Larsson (1964)
Ni_2P	hexagonal	$P\bar{6}2\,m$	5.859(2)	–	3.382(1)	Larsson (1964)

Note: standard deviations (1σ) are given in parentheses

2.4. Co-Ni-P system

No phase diagram of the system is available in the literature. Sénateur *et al.* (1973) reported a ternary phase with the composition CoNiP. In the Co-rich portion of the $(Ni,Co)_2P$ solid solution, Roger *et al.* (1969) described an orthorhombic phase with the composition $Co_{60}Ni_7P_{33}$. Phase relations in the Co_2P-Ni_2P system were investigated by Roger *et al.* (1969) and Fruchart *et al.* (1969). These authors presented a very broad hexagonal nickel-rich $(Co_{1-x}Ni_x)_2P$ solid solution and a restricted orthorhombic $(Co_{1-x}Ni_x)_2P$ solid solution. Villars *et al.* (1995) designated the hexagonal solid solution as λ_1 and the orthorhombic solid solution as λ_2. Solid solutions within the system at 800 °C have recently been reported by Drábek (2006). According to his results, the λ_1 solid solution spans from 0 to 75 mol. % Co_2P and the λ_2 solid solution spans from 83 to 100 mol. % Co_2P. The two-phase field $\lambda_1 + \lambda_2$ is quite narrow, ~8 mol. % Co_2P. At 800 °C, the solid solution $(Ni,Co)_{12}P_5$ dissolves 28.2 at. % Co whereas the $(Ni,Co)_5P_2$ solid solution dissolves only 1.8 at. % Co (Drábek, 2006). A broad solid solution between Ni_3P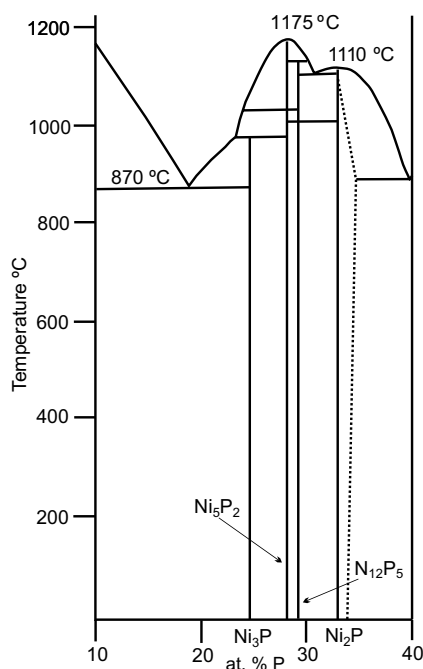 and "Co_3P" has been reported by Liu *et al.* (1998). This solid solution extends up to 52 mol. % Co_3P, and the unit-cell volumes deviate from Vegard's law (Drábek, 2006).

3. Experimental

Experiments were performed in evacuated and sealed silica glass tubes in horizontal tube furnaces (Kullerud, 1971). To prevent loss of material to the vapour phase during experiments, the free space in the tubes was reduced by placing closely fitting glass rods over the charge. The temperatures were measured with Pt-PtRh thermocouples and are accurate to ± 3 °C. The digital thermometer was periodically calibrated against the melting point of ice. The 800 °C isothermal section was selected because of reasonable reaction kinetics at this temperature. Charges 50–100 mg were weighed out from native elements or pre-synthesized binary compounds. Starting chemicals were cobalt powder (Koch-Light Laboratory, 99.5 % purity), nickel powder 99.999 (SPEX Inc.) and red phosphorus lump, 99.999 % (Aldrich Chem. Co). Cobalt and nickel react with phosphorus rapidly; nevertheless run times in some experiments were longer than necessary to reach en equilibrium. To facilitate the reactions, run products were repeatedly (1–3 times) reground under acetone and re-heated to 800 °C. After each run, the silica tubes were quenched in ice water. No phosphates, in-

Fig. 1. Schematized metal-rich portion of the Co-P system after Ishida & Nishizawa (1992).
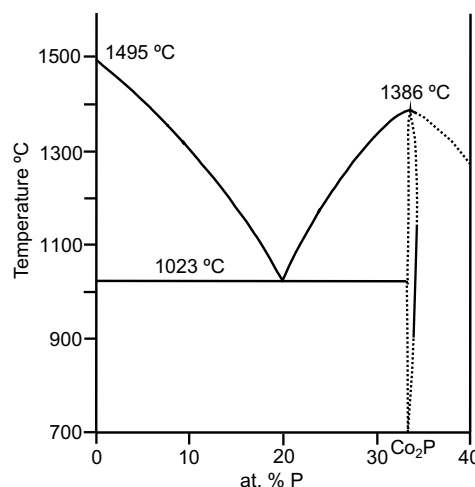

Fig. 2. Schematized diagram of the metal-rich portion of the Ni-P system after Lee & Nash (1992).

Table 2. Representative experiments in the Co-Ni-P system at 800 °C.

run No.	starting mixtures at. %			hours	products
	Co	Ni	P		
P77	30.77	38.46	30.77	620	λ_1-(Ni,Co)$_2$P+(Ni,Co)$_{12}$P$_5$
P94	31.43	40.00	28.57	141	(Ni,Co)$_{12}$P$_5$+(Ni,Co)$_3$P+λ_1-(Ni,Co)$_2$P
P100	13.33	60.00	26.67	620	(Ni,Co)$_3$P+(Ni,Co)$_{12}$P$_5$
P152	55.55	11.11	33.33	24	λ_2-(Co,Ni)$_2$P
P174	50.00	25.00	25.00	187	λ_1-(Ni,Co)$_2$P+(Ni,Co)$_3$P+α-(Co,Ni)
P176	35.71	35.71	28.57	118	(Ni,Co)$_{12}$P$_5$+λ_1-(Ni,Co)$_2$P+(Ni,Co)$_3$P
P182	42.86	31.14	25	450	λ_1-(Ni,Co)$_2$P+(Ni,Co)$_3$P+α-(Co,Ni)
P184	52.29	14.38	33.33	416	λ_1-(Ni,Co)$_2$P+λ_2-(Co,Ni)$_2$P
P197	45.71	25.71	28.57	739	λ_1-(Ni,Co)$_2$P+(Ni,Co)$_3$P+α-(Co,Ni)[*]
P216	55.00	15.00	30.00	427	(Ni,Co)$_3$P+α-(Co,Ni)
P217	64.29	7.14	28.57	340	λ_2-(Co,Ni)$_2$P+α-(Co,Ni)[**]
P256	28.42	42.35	29.41	750	(Ni,Co)$_{12}$P$_5$
P259	5.00	66.43	28.57	270	(Ni,Co)$_{12}$P$_5$+(Ni,Co)$_3$P
P268	4.55	68.18	27.27	30	(Ni,Co)$_3$P+(Ni,Co)$_{12}$P$_5$
P269	22.73	50.00	27.27	270	(Ni,Co)$_3$P+(Ni,Co)$_{12}$P$_5$
P272	60.00	20.00	20.00	1480	λ_1-(Ni,Co)$_2$P+(Ni,Co)$_3$P+α-(Co,Ni)[***]
P273	20.00	60.00	20.00	1500	(Ni,Co)$_3$P+α-(Co,Ni)
P274	1.82	70.91	27.27	1500	(Ni,Co)$_5$P$_2$+(Ni,Co)$_3$P
P280	37.50	37.50	25	1300	(Ni,Co)$_3$P
P315	39.84	38.16	25	160	λ_1-(Ni,Co)$_2$P+(Ni,Co)$_3$P+α-(Co,Ni)
P320	1.86	69.71	28.57	1000	(Ni,Co)$_5$P$_2$+>>Ni$_{12}$P$_5$
P329	3.64	69.09	27.27	320	(Ni,Co)$_{12}$P$_5$+(Ni,Co)$_5$P$_2$+(Ni,Co)$_3$P
P335	2.51	68.92	28.57	776	(Ni,Co)$_{12}$P$_5$+(Ni,Co)$_5$P$_2$+(Ni,Co)$_3$P
P348	49.65	17.02	33.33	440	λ_1-(Ni,Co)$_2$P

[*] 22.7 at. % Ni; [**] 21.8 at. % Ni; [***] 7 at. % Ni

dicating a poor vacuum or oxidation during grinding, were observed. Run products are fine-grained (including metal particles) and form intimate intergrowths. No eutectoid textures were observed. Optical properties of synthesized phosphides are similar. The possibilities of optical and microprobe identification of the phases present were limited, with the exception of the composition of metallic phases. Thus, X-ray diffraction was the most reliable technique used to determine phase compositions of run products, including the extent of solid solutions. Philips X'Pert MPD system with a vertical goniometer PW3020 in the Bragg-Brentano reflecting geometry, copper radiation (40 kV and 40 mA), secondary graphite monochromator and a proportional counter were used to collect X-ray powder data. The samples were placed on a low-background silicon holder. Step-scanned data were collected in the angular range 20–145° 2θ with step size 0.02° and 8 seconds exposure per step.

The whole profile-fitting method (WPPF) was applied to calculate unit-cell parameters from powder data. The program used for calculations was FullProf (Rodríguez-Carvajal, 2001). Chemical analyses of α-(Co,Ni) alloys were carried out on a Cameca SX-100 microprobe in the wavelength-dispersion mode.

4. Experimental results

Only relevant experiments (selected from a total of 150 runs) are given in Table 2. Based on the literature data (Nishizawa & Ishida, 1992; Ishida & Nishizawa, 1992; Lee & Nash, 1992; Drábek, 2006) and on additional experiments,

the 800 °C "condensed" isothermal section (stable assemblages coexisting with a vapour phase, not shown) for the Co-Ni-P system is presented in Fig. 3. From the phase diagram, it is obvious that five ternary phosphorus-containing solid solutions dominate the system at this temperature: 1) nickel-rich hexagonal, λ_1-(Ni$_{1-x}$Co$_x$)$_2$P solid solution; 2) cobalt-rich orthorhombic, λ_2-(Co$_{1-x}$Ni$_x$)$_2$P solid solution, 3) tetragonal, (Ni$_{1-x}$Co$_x$)$_{12}$P$_5$ solid solution; 4) hexagonal (Ni$_{1-x}$Co$_x$)$_5$P$_2$ solid solution and 5) tetragonal, (Ni$_{1-x}$Co$_x$)$_3$P solid solution. Furthermore, binary inter-metallic α-(Co,Ni) solid solution is present in the system.

At 800 °C, eleven assemblages were found to be stable in the metal-rich portion of the Co-Ni-P system:

1) λ_1-(Ni$_{1-x}$Co$_x$)$_2$P s.s. + (Ni$_{1-x}$Co$_x$)$_{12}$P$_5$ s.s.
2) (Ni$_{1-x}$Co$_x$)$_{12}$P$_5$ s.s. + (Ni$_{1-x}$Co$_x$)$_5$P$_2$ s.s.
3) (Ni$_{1-x}$Co$_x$)$_5$P$_2$ s.s. + (Ni$_{1-x}$Co$_x$)$_3$P s.s.
4) (Co$_{1-x}$Ni$_x$)$_3$P s.s. + (Ni$_{1-x}$Co$_x$)$_{12}$P$_5$ s.s. + (Ni$_{1-x}$Co$_x$)$_5$P$_2$ s.s.
5) (Co$_x$Ni$_{1-x}$)$_{12}$P$_5$ s.s. + (Ni$_{1-x}$Co$_x$)$_3$P s.s.
6) α-(Co,Ni) s.s. + (Ni$_{1-x}$Co$_x$)$_3$P s.s.
7) λ_1-(Ni$_{1-x}$Co$_x$)$_2$P s.s. + (Ni$_{1-x}$Co$_x$)$_3$P s.s. + (Ni$_{1-x}$Co$_x$)$_{12}$P$_5$ s.s.
8) α-(Co,Ni) s.s. + λ_1-(Ni$_{1-x}$Co$_x$)$_2$P s.s. + (Ni$_{1-x}$Co$_x$)$_3$P s.s.
9) α-(Co,Ni) s.s. + λ_1-(Ni$_{1-x}$Co$_x$)$_2$P s.s.
10) α-(Co,Ni) s.s. + λ_1-(Ni$_{1-x}$Co$_x$)$_2$P s.s. + λ_2-(Ni$_{1-x}$Co$_x$)$_2$P s.s.
11) α-(Co,Ni) s.s. + λ_2-(Co$_{1-x}$Ni$_x$)$_2$P s.s.
(s.s. = solid-solution)

There is an incomplete solid solution between Co$_2$P and Ni$_2$P. The two-phase λ_1 + λ_2 region is relatively narrow, it spans ~8 mol. % Co$_2$P. The nickel-rich λ_1-(Ni$_{1-x}$Co$_x$)$_2$P sol-
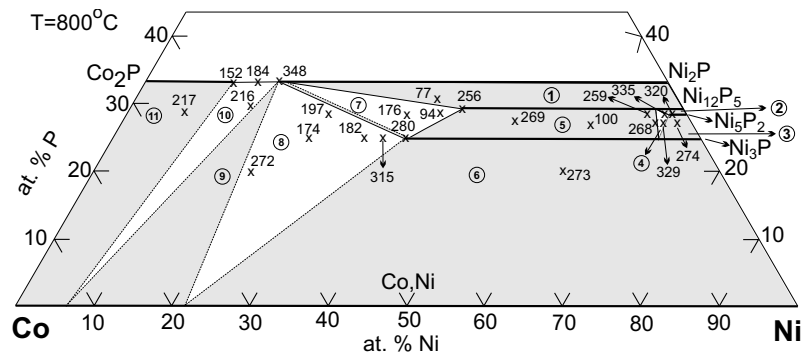
Fig. 3. The 800 °C isotherm of the metal-rich portion of the Co-Ni-P system. Compositions of important experiments are shown and numbered. Circled numbers indicate separate stable assemblages present in the system.

Table 3. Lattice parameters of the end compositions of ternary solid solutions.

run No.	phase	a [Å]	b [Å]	c [Å]	V [Å³]
P33/3*	Ni_3P	8.9549(1)	–	4.3873(1)	351.82(1)
P280	$(Co_{0.50}Ni_{0.80})_3P$	8.9577(1)	–	4.3789(1)	351.37(1)
P17**	λ_2-Co_2P	5.6490(3)	3.5126(2)	6.6071(3)	131.11(1)
P152	λ_2-$(Co_{0.84}Ni_{0.16})_2P$	5.6772(2)	3.4973(4)	6.6174(4)	131.39(1)
P255	$Ni_{12}P_5$	8.6447(1)	–	5.0702(1)	378.89(1)
P256	$Co_{4.8}Ni_{7.2}P_5$	8.6108(1)	–	5.0573(1)	374.97(1)
P75***	λ_1-Ni_2P	5.8661(4)	–	3.3877(1)	100.96(2)
P348	λ_1-$Co_{1.49}Ni_{0.51}P$	5.8044(2)	–	3.3852(2)	98.77(2)

Note: standard deviations (1σ) are given in parentheses

* Skála & Drábek (2000); ** Skála & Drábek (2001); *** Drábek & Skála (2002)

id solution extends to the composition $Co_{1.49}Ni_{0.57}P$ (47.7 at. % Co) and the cobalt-rich λ_2-$(Co_{1-x}Ni_x)_2P$ extends only to the composition $Co_{1.67}Ni_{0.33}P$ (56 at. % Co). The $(Ni_{1-x}Co_x)_3P$ solid solution is limited (the phase Co_3P is not stable) and extends only up to the composition $Co_{1.5}Ni_{1.5}P$ (37.5 at. % Co). The $(Ni_{1-x}Co_x)_{12}P_5$ solid solution reaches the composition $Co_{4.8}Ni_{7.2}P_5$ (28.2 at. % Co) and the $(Ni_{1-x}Co_x)_5P_2$ solid solution dissolves only up to 1.9 at. % Co.

Phosphides λ_1-$(Ni,Co)_2P$, λ_2-$(Co,Ni)_2P$ and $(Ni,Co)_3P$ form stable assemblages with the inter-metallic α-(Co,Ni) solid solution. According to microprobe analyses, the cobalt-rich λ_2-$(Co~Ni~)_2P$ solid solution forms stable assemblages with α-(Co,Ni) solid solution containing up ~7 at. % Ni. The cobalt-rich end member of λ_1-$(Ni_{1-x}Co_x)_2P$ solid solution is stable with α-(Co,Ni) with a composition ranging from ~7 to 22 at. % Ni, and the $(Ni_{1-x}Co_x)_3P$ solid solution forms a stable assemblage with the α-(Co,Ni) solid solution containing ~22–100 at. % Ni.

The substitution of nickel by cobalt is accompanied by a slight decrease in the unit-cell volume (Table 3). The difference between unit cell volumes of the end compositions of $(Ni_{1-x}Co_x)_3P$ solid solution is very small, only 0.1 %. The difference between unit-cell volumes of end compositions of λ_1-$(Ni,Co)_2P$ and λ_2-$(Co,Ni)_2P$ solid solution reaches 2.2 % and 0.2 %, respectively. The difference between the unit cell-volume of end compositions of the $(Ni,Co)_{12}P_5$ solid solution is 1 %. Variations of unit cell-volumes of $(Ni,Co)_3P$, λ_1-$(Ni,Co)_2P$ and $(Ni,Co)_{12}P_5$ solid solution with cobalt contents are presented in Fig. 4. From the figure it is

obvious that the variation of unit-cell volumes of $(Ni,Co)_3P$ and λ_1-$(Ni,Co)_2P$ solid solutions with cobalt is non-linear and deviates from Vegard's law. A 2nd order polynomial fit must be applied to express this variation. Contrariwise, the variation of unit-cell volumes of $(Ni,Co)_{12}P_5$ solid solution with cobalt is linear.

5. Conclusions

The system studied differs from the analogous Co-Fe-P system (Berak, 1951). These differences follow primarily from the distinct phase relations within the marginal Ni-P and Co-Ni systems. The present experiments within the marginal Ni-P system confirm, in agreement with data of Lee & Nash (1992), the stability of four binary phases: Ni_3P, Ni_5P_2, $Ni_{12}P_5$, and Ni_2P. Further four broad ternary solid solutions were identified in the system. $(Ni,Co)_3P$, λ_1-$(Ni,Co)_2P$ and λ_2-$(Co,Ni)_2P$ solid solutions form stable assemblages with the α-(Co,Ni) alloy. Contrariwise, $(Ni,Co)_{12}P_5$, $(Ni,Co)_5P_2$ solid solutions do not form stable assemblages with the α-(Co,Ni) alloy.

The substitution of nickel by cobalt is associated with a decrease in unit-cell volumes. The observed anomalous behaviour of unit-cell volumes of $(Ni,Co)_3P$ and λ_1-$(Ni,Co)_2P$ solid solutions could be explained by three non-equivalent structure sites in their crystal structures (Liu et al., 1998). According to Fruchart et al. (1969) and Skála & Drábek (1999) the coordination polyhedra around these sites have different volumes. Therefore, the preferential occupancy of these structure
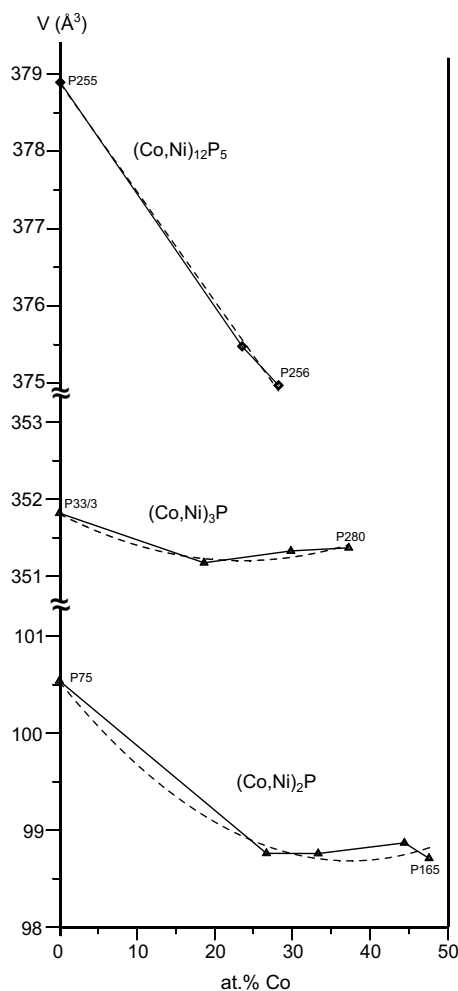
Fig. 4. Variation of unit-cell volumes of $(Ni,Co)_3P$, λ_1-$(Ni,Co)_2P$ and $(Ni,Co)_{12}P_5$ solid solutions with their cobalt content. Symbols indicate results from WPPF. Data for $(Ni,Co)_3P$, λ_1-$(Ni,Co)_2P$ are fitted with 2nd order polynominal and data for $(Ni,Co)_{12}P_5$ are fitted linearly.

sites by cobalt or nickel described by Liu *et al.* (1998) may explain the observed anomalous unit-cell volume variation.

The occurrence of cobalt-dominant phases in nature is uncertain at best, but cobalt-containing Ni-rich phosphides, isotypic with minerals allabogdanite or schreibersite and phosphides with Ni/P ratios 12:5 and 5:2 might possibly be found in Co- and Ni-rich meteorites. Nevertheless, 12:5 and 5:2 nickel phosphides are not to be expected to occur in association with metallic phases.

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