Solid Solutions of the Type $(Ni,M)_2P_2O_7$

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Solid solutions $(Ni,M)_2P_2O_7$ have been prepared (M = Mg, Mn, Fe, Co, Cu or Zn). The α- and δ-$Ni_2P_2O_7$ structure types have been identified. Accurate unit cell dimensions are given. The solubility in $Ni_2P_2O_7$ is large (100 %) for Mg and Co, moderate for Fe, Cu and Zn, and small for Mn. The extension of the solubility region is for each (Ni,M)-diphosphate series mainly controlled by cation sizes. Mössbauer data (^{57}Fe) are given for the (Ni,Fe) diphosphates.

Since 1980 we have undertaken extensive studies of solid solutions of divalent-metal (M^{2+}) oxosalt compounds, mainly to correlate various crystallographic properties. So far orthophosphates have principally been investigated.[1–4] Recently we have expanded our studies to diphosphates.[5–7] The present paper reports on phases of the type $(Ni,M)_2P_2O_7$.

The crystal structure of the thermodynamically stable room-temperature modification α-$Ni_2P_2O_7$ ($B2_1/c$, Z = 8) was determined in 1967 by Lukaszewicz.[8] This structure contains 5- and 6-coordinated metal cations. Three further polymorphs have been reported: a high-temperature β-phase ($C2/m$, Z = 2) with the thortveitite structure (six-coordinated metal atoms),[9] a γ-phase (denoted α′ by Lukaszewicz),[8] probably isomorphous with α-$Zn_2P_2O_7$, which has the metal coordination numbers 5, 5 and 6 ($I2/c$, Z = 12), and a δ-phase[10] ($P2_1/a$, Z = 2) with six-coordinated metal cations. The basic α-modification is usually preserved when Ni^{2+} is replaced by smaller amounts of an equi-sized cation M^{2+}. Sometimes the δ-form is instead formed (cf. below).

Experimental

Pure diphosphates and solid solutions $(Ni_{1-x}M_x)_2P_2O_7$ were prepared at 800 °C (1070 K) as described earlier.[1,5] However, $Fe_2P_2O_7$ was prepared from 85 % orthophosphoric acid and metallic iron powder in a protective argon atmosphere. The mixture was heated to 420 °C, at which temperature iron(II) metaphosphate was first formed, whereupon continued heating at 800 °C gave $Fe_2P_2O_7$.

The samples were analyzed with a JEOL JSM-840 scanning electron microscope and a LINK-EDX, as well as by X-ray powder diffraction (Guinier camera, Cu $K\alpha_1$ radiation, KCl internal standard). The Guinier photographs were evaluated with a computer-controlled film scanner and associated programs.[11]

^{57}Fe Mössbauer data of the (Ni,Fe) diphosphates were recorded in transmission geometry with an electromechanical Doppler velocity generator operating at constant acceleration mode (512 channels per spectrum). The folded spectra (256 channels) were fitted by the least-squares method with Lorentzian functions, without thickness correction: the samples contained less than 5 mg natural iron per cm^2. The centroid shifts (CS) are given relative to α-Fe at room temperature, and the quadrupole splitting (QS) is defined as the peak separation in the doublet.

Results

Unit-cell dimensions and approximate homogeneity ranges are given in Table 1. The e.s.d. values are usually large for compositions close to the upper homogeneity limits, indicating the approaching breakdown of the respective structure. In the discussion below, the cited cation radii are those published by Shannon[12] for an octahedral environment of oxygen atoms. The radius for Ni^{2+}, r_{Ni}, is 0.69 Å.

Mg^{2+} (r = 0.72 Å) and Co^{2+} (r = 0.745 Å) are completely soluble in α-$Ni_2P_2O_7$ over the whole composition range. This accords very well with the established isomorphism between the α-diphosphates of Mg, Co, and Ni (cf. Ref. 13).

Cu^{2+} (r = 0.73 Å) and Zn^{2+} (r = 0.74 Å) are moderately soluble in α-$Ni_2P_2O_7$. When Fe^{2+} (r = 0.78 Å) was substituted for nickel, the Guinier photographs turned out to be very diffuse for compositions up to about 10 % Fe (atom percent of the total metal contents). The δ-phase is formed at least in the interval 10–20 % Fe, thereafter the α-modification shows up with an observed maximum solubility of ~ 70 % Fe. There is a discontinuity in the $V/Z = f(x)$ graph for the $(Ni_{1-x}Fe_x)_2P_2O_7$ solid solution series at $x \approx 0.25$, as the crystal structure changes from δ to the less closely packed α-structure. (Z is the number of formula units per unit cell.)

Mn^{2+} (r = 0.83 Å) is the largest cation to allow replacement of the small Ni^{2+} ion. The solubility is rather small,

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Table 1. Unit-cell dimensions for the $(Ni,M)_2P_2O_7$ solid solutions. α-Ni_{100} stands for α-$Ni_2P_2O_7$, α-$Ni_{80}Mg_{20}$ for α-$(Ni_{0.80}Mg_{0.20})_2P_2O_7$, and so forth.

Phase	*a*/Å	*b*/Å	*c*/Å	*β*/°	*V*/Å^3
α-Ni_{100}	13.123(3)	8.268(2)	8.971(3)	104.79(3)	941.1(5)
α-$Ni_{80}Mg_{20}$	13.128(5)	8.271(3)	8.988(4)	104.82(4)	943.5(9)
α-$Ni_{60}Mg_{40}$	13.163(5)	8.279(4)	9.007(6)	104.85(5)	948.8(10)
α-$Ni_{50}Mg_{50}$	13.176(4)	8.282(2)	9.017(4)	104.90(3)	950.9(6)
α-$Ni_{40}Mg_{60}$	13.182(5)	8.286(3)	9.033(3)	105.01(4)	952.9(7)
α-$Ni_{20}Mg_{80}$	13.216(4)	8.288(4)	9.042(4)	104.98(5)	956.7(8)
α-Mg_{100}	13.240(4)	8.291(2)	9.050(3)	104.65(3)	961.0(6)
α-$Ni_{90}Cu_{10}$	13.123(7)	8.278(5)	8.979(5)	104.83(6)	942.9(12)
α-$Ni_{80}Cu_{20}$	13.126(6)	8.288(4)	8.983(4)	104.89(5)	944.4(11)
α-$Ni_{70}Cu_{30}$	13.129(8)	8.302(7)	8.989(6)	105.07(7)	946.1(15)
α-$Ni_{60}Cu_{40}$	13.133(11)	8.313(9)	8.994(9)	105.14(8)	947.8(17)
α-$Ni_{90}Zn_{10}$	13.150(6)	8.271(4)	8.974(5)	104.64(4)	944.3(8)
α-$Ni_{80}Zn_{20}$	13.171(7)	8.275(6)	8.987(5)	104.57(5)	948.0(12)
α-$Ni_{70}Zn_{30}$	13.195(10)	8.285(8)	8.994(7)	104.51(7)	951.9(16)
α-$Ni_{65}Zn_{35}$	13.216(12)	8.291(10)	9.003(10)	104.47(8)	955.2(19)
α-$Ni_{75}Co_{25}$	13.148(4)	8.282(2)	8.976(3)	104.73(4)	945.3(7)
α-$Ni_{50}Co_{50}$	13.182(6)	8.303(4)	8.984(3)	104.69(4)	951.2(8)
α-$Ni_{25}Co_{75}$	13.213(5)	8.322(3)	8.992(4)	104.69(3)	956.4(8)
α-Co_{100}	13.249(3)	8.341(2)	9.003(2)	104.64(2)	962.6(6)
δ-Ni_{100}	5.212(2)	9.914(3)	4.467(2)	97.50(3)	228.8(3)
δ-$Ni_{90}Fe_{10}$	5.227(2)	9.918(3)	4.471(3)	97.49(4)	229.8(3)
δ-$Ni_{80}Fe_{20}$	5.240(2)	9.931(4)	4.471(2)	97.44(3)	230.7(3)
α-$Ni_{75}Fe_{25}$	13.170(3)	8.262(3)	8.987(3)	104.77(4)	945.6(4)
α-$Ni_{70}Fe_{30}$	13.178(4)	8.299(4)	8.991(5)	104.81(3)	950.7(8)
α-$Ni_{60}Fe_{40}$	13.191(6)	8.372(5)	8.999(8)	104.91(8)	960.3(14)
α-$Ni_{50}Fe_{50}$	13.213(12)	8.426(8)	9.108(10)	105.07(11)	979.1(20)
α-$Ni_{40}Fe_{60}$	13.232(9)	8.503(8)	9.115(8)	105.16(9)	989.9(16)
α-$Ni_{30}Fe_{70}$	13.256(13)	8.517(9)	9.129(10)	105.22(10)	994.5(22)
δ-$Ni_{95}Mn_{05}$	5.216(3)	9.924(4)	4.472(3)	97.51(3)	229.5(4)
δ-$Ni_{90}Mn_{10}$	5.221(5)	9.933(7)	4.479(5)	97.54(4)	230.3(6)

around 10 %. As far as we have observed, only the δ-modification is formed. Cd^{2+} (r = 0.95 Å) and Ca^{2+} (r = 1.00 Å) are too large to enter the nickel(II) diphosphate structure.

All M^{2+} cations studied here are larger than Ni^{2+}. When any of these is substituted for nickel in $Ni_2P_2O_7$, the cell axis length increases. Generally, the relative increase is most noticeable for the *a* axis, but in the (Ni,Cu) and α-(Ni,Fe) series the monoclinic *c* axis instead displays the largest increase. The cell volumes *V* of the α-$(Ni,M)_2P_2O_7$ series as a function of the composition are shown in Fig. 1. The graphs are roughly linear, except for the (Ni,Fe) diphosphates.

The $\delta \rightarrow \alpha$ phase transition in $(Ni,Fe)_2P_2O_7$ is clearly observed in the Mössbauer spectra. The room-temperature (RT; $\approx$ 295 K) spectrum for the δ-phase only contains one symmetrical doublet with CS $\approx$ 1.23 mm s^{-1} and QS $\approx$ 2.44 mm s^{-1} (Fig. 2). The parameters at liquid-nitrogen temperature (LNT; 77 K) are CS $\approx$ 1.34 mm s^{-1} and QS $\approx$ 2.89 mm s^{-1}. Accordingly, the change in CS is almost exactly as expected from the second-order Doppler shift.

For iron contents around 25–70 % of the metal contents, the α-structure is formed. The Mössbauer spectra contain two doublets (Fig. 3) emanating from the five- and six-coordinated metal sites in the structure. The low-velocity profile at $\approx$ 0 mm s^{-1} in the RT spectrum is clearly resolved into two peaks, but the high-velocity profile does not show any internal structure due to closely overlapping peaks. The intensities of the two doublets are roughly the same.

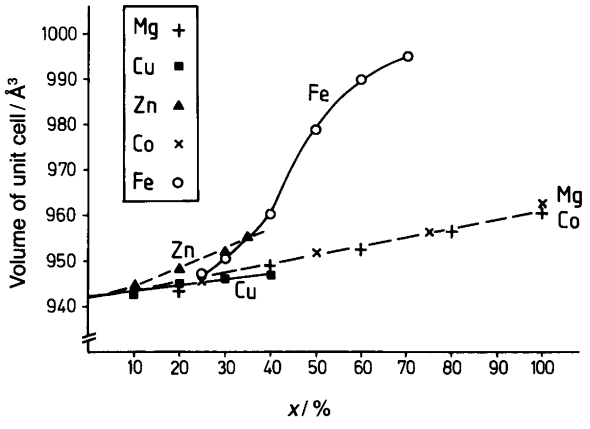

Fig. 1. Unit-cell volume *V* (Å^3) versus composition *x* (in atom %) for various α-$(Ni_{1-x}M_x)_2P_2O_7$ solid solutions. The unit cell contains eight formula units. The lines are hand-drawn and only guides to the eye. Note that there is a change in structure from δ to α for the (Ni,Fe) diphosphates.

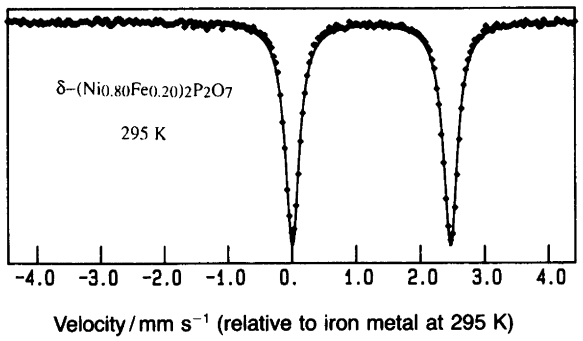

Fig. 2. Mössbauer spectrum of δ-$(Ni_{0.80}Fe_{0.20})_2P_2O_7$ recorded at 295 K. The velocity (mm s^{-1}) is given relative to α-Fe at 295 K.

Accordingly, iron and nickel occupy the two positions in a random way. This is logical, since the samples were prepared at 800 °C, where β-$Ni_2P_2O_7$ is the thermodynamically stable phase, having only one crystallographically distinct metal site. When quenched, the random distribution from the β-phase is preserved in the α-phase.

It is possible to assign the two doublets of the RT spectrum of α-$(Ni_{0.30}Fe_{0.70})_2P_2O_7$ in two ways: either with crossed doublets giving CS(1) = 1.10, QS(1) = 2.48, CS(2) = 1.33 and QS(2) = 2.35 mm s^{-1}, or with overlapping doublets to give CS(1) = 1.18, QS(1) = 2.65, CS(2) = 1.24 and QS(2) = 2.19 mm s^{-1}. By comparing RT and LNT spectra, it is most simple to assume variations in CS as emanating principally from the second-order Doppler shift. Thus the CS values at 77 K should be around 0.1 mm s^{-1} larger than at RT. Using this hypothesis and comparing RT and LNT spectra (Fig. 3), it is obvious that only the model with overlapping doublets gives acceptable fits. The Mössbauer parameters for the (Ni,Fe) diphosphates are given in Table 2.

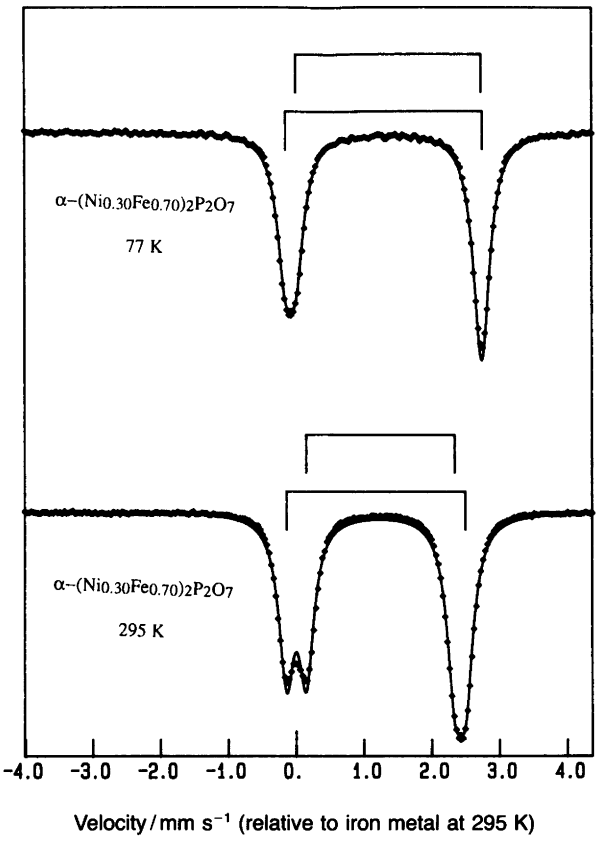

Fig. 3. Mössbauer spectrum of α-$(Ni_{0.30}Fe_{0.70})_2P_2O_7$ recorded at liquid-nitrogen temperature (above) and at room temperature (below). The bars indicate the positions of the two overlapping doublets. For more details, see the text.

Table 2. Mössbauer parameters recorded at 295 K (RT) and 77 K (LNT) for the $(Ni,Fe)_2P_2O_7$ solid solutions. $Ni_{90}Fe_{10}$ stands for $(Ni_{0.90}Fe_{0.10})_2P_2O_7$, and so forth.

Composition	T/K	Position 1		Position 2	
		CS/mm s^{-1}	QS/mm s^{-1}	CS/mm s^{-1}	QS/mm s^{-1}
δ-$Ni_{90}Fe_{10}$	295	1.23	2.44		
δ-$Ni_{80}Fe_{20}$	295	1.24	2.47		
α-$Ni_{75}Fe_{25}$	295	1.21	2.55	1.23	2.27
α-$Ni_{70}Fe_{30}$	295	1.19	2.55	1.26	2.36
α-$Ni_{60}Fe_{40}$	295	1.18	2.75	1.25	2.24
α-$Ni_{50}Fe_{50}$	295	1.19	2.75	1.26	2.24
α-$Ni_{40}Fe_{60}$	295	1.19	2.78	1.25	2.23
α-$Ni_{30}Fe_{70}$	295	1.18	2.65	1.24	2.19
δ-$Ni_{80}Fe_{20}$	77	1.34	2.89		
α-$Ni_{30}Fe_{70}$	77	1.30	2.93	1.37	2.76

The intensities of the two α-structure positions are the same (± 2 %). CS is given relative to α-Fe at RT (precision ± 0.01 mm s^{-1}), and the precision of QS is ± 0.02 mm s^{-1}.

Discussion

In this study, as well as in our earlier investigations of solid solutions, the cell volume is clearly correlated with the size and amount of incorporated M^{2+} cations (Fig. 1). However, it is also of interest to correlate the extensions of the solubility regions with some crystallographic properties. Sometimes the homogeneity ranges are principally controlled by cation site preferences (e.g. Ref. 4). With regard to the α-$(Mg,M)_2P_2O_7$ diphosphates, the M^{2+} sizes mainly determine the extensions of the solubility regions.[6] To facilitate comparisons between M^{2+} solubilities in $Ni_2P_2O_7$, $Mg_2P_2O_7$ and $Mn_2P_2O_7$, some data are summarized in Table 3.

It is obvious from Table 3 that the maximum homogeneity ranges for α-$(Ni,M)_2P_2O_7$ resemble those of corresponding α-$(Mg,M)_2P_2O_7$ series,[6] although with M = Fe as the only outstanding exception. Accordingly, the $(Ni,M)_2P_2O_7$ homogeneity ranges are mainly controlled by cation sizes as in $(Mg,M)_2P_2O_7$,[6] but to some extent also by similarities between the $Ni_2P_2O_7$ and $M_2P_2O_7$ structures.

However, the large solubility of Fe^{2+} in $Ni_2P_2O_7$ can be explained neither from equi-sized cations nor from structural similarities between the respective diphosphate structures. For compositions having around 10–20 atom % Fe (of the total metal contents), the more densely packed δ-structure is formed upon quenching of a high-temperature β-$(Ni,Fe)_2P_2O_7$ phase. For larger amounts of Fe, about 25–70 atom %, the less closely packed α-structure is formed instead. The pronounced Fe^{2+} tendency for five-coordination[4] may explain this large ability of divalent iron to enter the α-$Ni_2P_2O_7$ structure. In this region the unit-cell volume increases continuously with iron content (Fig. 1). On the other hand, an extrapolation to 0 % Fe gives a hypothetical unit-cell volume around 921 Å,^{3} i.e. ≈ 20 Å^3 *smaller* than the observed unit-cell volume for pure α-$Ni_2P_2O_7$ (941.1 Å;^{3} Table 1). Thus there are indications that the α-$(Ni,Fe)_2P_2O_7$ phases at 25–70 % Fe may not be strictly isostructural with pure α-$Ni_2P_2O_7$, even if our X-ray and Mössbauer data do not show any signs of a superstructure or any other structural discrepancy or disorder in the α-$(Ni,Fe)_2P_2O_7$ phases.

As regards Ni^{2+} itself, it is curious that the α-$Ni_2P_2O_7$ structure be formed at all. Five-coordinated divalent nickel is indeed rare, and has only been definitely verified in the α-$Ni_2P_2O_7$ structure,[8] although it is also likely to occur in $Ni_2(PO_4)F$,[14] isostructural with the mineral wagnerite, $Mg_2(PO_4)F$.[15] Partly for these reasons, further studies to establish cation partitionings in $(Ni,M)_2P_2O_7$ phases will be undertaken by means of Mössbauer spectroscopy, diffraction techniques and electronic (optical) spectroscopy.

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Table 3. Maximum solubilities, in atom % of the total metal contents, for various M^{2+} cations in three diphosphate structures. CN denotes the cation coordination number(s) in the respective structures. The cation radii are those of Shannon.[12]

Base structure:		α-$Ni_2P_2O_7$[a]	α-$Mg_2P_2O_7$[b]	$Mn_2P_2O_7$[c] (β-type)
CN:		5 + 6	5 + 6	6
M^{2+}	r_M/Å			
Ni	0.69	(100)	100	60
Mg	0.72	100	(100)	20
Cu	0.73	40	35	15
Zn	0.74	35	40	35
Co	0.745	100	100	15
Fe	0.78	70[d]	10	60
Mn	0.83	(10)[e]	5	(100)
Cd	0.95	0	0	15
Ca	1.00	0	0	5

[a]This work, [b]Ref. 6, [c]Ref. 5. [d]The α-modification is formed around 25–70 % Fe, but for 10–20 % Fe the δ-phase is obtained instead. [e]The $(Ni,Mn)_2P_2O_7$ phases crystallize with the δ-structure.

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