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Acta Cryst. (1981). B**37**, 1509–1511

A Neutron Diffraction Study of γ-$(Zn_{0.70}Ni_{0.30})_3(PO_4)_2$

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(*Received* 12 *November* 1980; *accepted* 9 *February* 1981)

Abstract

The solid solution γ-$(Zn_{0.70}Ni_{0.30})_3(PO_4)_2$ has been studied utilizing neutron powder diffraction data. The title compound is monoclinic, $P2_1/n$, with $a = 7{\cdot}505\,(1)$, $b = 8{\cdot}316\,(1)$, $c = 5{\cdot}056\,(1)$ Å, $\beta = 94{\cdot}48\,(1)^\circ$, $V = 314{\cdot}6\,(1)$ Å^3 and $Z = 2$. The structure has been refined utilizing the Rietveld full-profile refinement technique ($R_I = 0{\cdot}052$; 72 reflections), and the cation distribution between the five- and six-coordinated sites has been determined. Ni^{2+} is strongly ordered at the octahedral sites. These metal–oxygen octahedra (MO_6) are fairly regular, while the MO_5 polyhedra are distorted trigonal bipyramids.

Introduction

Pure zinc orthophosphate can exist in two forms: α-$Zn_3(PO_4)_2$ with tetrahedrally coordinated cations (Calvo, 1965), and β-$Zn_3(PO_4)_2$, stable above ~1200 K, containing five- and six-coordinated Zn ions (Stephens & Calvo, 1967). Experiments have shown that upon replacement of Zn in the α phase by Cd^{2+}, Mg^{2+} or Mn^{2+}, a solid solution may be formed known as 'γ-$Zn_3(PO_4)_2$', or preferably γ-$(Zn, M)_3(PO_4)_2$ (*e.g.* Kreidler & Hummel, 1967). Recent studies have verified that Co^{2+}, Fe^{2+}, Ni^{2+} or Cu^{2+} may also stabilize the γ phase with respect to α-$Zn_3(PO_4)_2$ (Nord & Kierkegaard, 1980).

The structure of 'γ-$Zn_3(PO_4)_2$' was determined by Calvo (1963). Two thirds of the cations occupy five-coordinated sites, henceforward called $M(1)$, while the rest reside in octahedral sites, $M(2)$. Calvo suggested that the incorporated cations should preferentially enter the $M(2)$ sites, thereby stabilizing the γ phase with respect to α-$Zn_3(PO_4)_2$. This idea has been supported by an X-ray powder diffraction study of γ-$Zn_2Mg(PO_4)_2$ by Nord (1977). Later the cation distribution in a series of γ-$(Zn,Fe)_3(PO_4)_2$ solid solutions was determined utilizing the Mössbauer effect (Annersten, Ericsson & Nord, 1980), again showing the strong ordering of Fe^{2+} at the $M(2)$ sites. These investigations were undertaken as part of a project on cation distributions in mineral and inorganic structures involving five-coordinated metal sites. In the present study neutron powder diffraction data have been used to determine the cation ordering in a γ-$(Zn,Ni)_3(PO_4)_2$ solid solution. 30 at.% Ni was used; this is close to the maximum solubility of Ni in the γ phase at about 1070 K.

Experimental

Pure orthophosphates of Zn and Ni were prepared by allowing stoichiometric amounts of $NH_4H_2PO_4$ and the respective metal oxide to react at 1200 K for two weeks. These phosphates were then mixed in the proportion 70:30 and heated to about 1070 K. The sample was quenched and ground once every week to ensure complete homogeneity as well as equilibrium. The heating continued for three months; the sample was finally quenched to room temperature.

X-ray powder data were obtained at 298 K with a Guinier–Hägg-type focusing camera (Cu $K\alpha_1$ radiation, $\lambda = 1{\cdot}54050$ Å, KCl internal standard) and the photograph evaluated by a film scanner and associated programs (Malmros & Werner, 1973).

0567-7408/81/081509-03$01.00

Neutron powder diffraction data were collected at the Studsvik *R*2 reactor from 3 cm^3 (~10 g) of powdered sample, using a double monochromator in parallel setting (Cu crystals). The average flux was 10^{10} neutrons $m^{-2}\,s^{-1}$ for $\lambda \simeq 1\cdot56$ Å. Accurate data were collected for $2 \le \theta \le 30°$ with a total scan time of 5 d ($\Delta\theta = 0\cdot04°$); for $\theta > 30°$ the reflections overlapped to a high degree and it was difficult to fix the background level.

Profile refinements

The intensity profile contained a total of 72, partly overlapping independent Bragg reflections. The profile of each reflection (as *I v θ*) had an almost perfectly symmetric Gaussian shape. After subtraction of the graphically determined background, the intensity data were processed by means of the full-profile refinement procedure by Rietveld (1969). In a preliminary step the scale factor, zero point, and unit-cell dimensions were refined, thus fixing the mean neutron wavelength to 1·5594 (3) Å. The complete structure was then refined with 23 parameters: one scale factor *C* such that $I_{calc} = C.I_{obs}$, three intensity-profile parameters, 18 atomic positional parameters, and an isotropic overall temperature factor. Space group $P2_1/n$ (No. 14) was assumed, after Calvo (1963, 1973).

The cation distribution was expressed by a parameter *x*, which is defined by γ-$(Zn_{1-x}Ni_x)_2^{M(1)}$-$(Zn_{0\cdot1+2x}Ni_{0\cdot9-2x})^{M(2)}(PO_4)_2$, with $0 \le x \le 0\cdot45$. Thus $x = 0$ indicates an 'ordered' situation with all *M*(1) sites occupied by Zn, while $x = 0\cdot30$ gives a random distribution of the cations. The value of *x* was determined through a series of refinements with shifted *x* values. Neutron scattering amplitudes were taken from *International Tables for X-ray Crystallography* (1968). The discrepancy index R_I, defined as $\sum|I_{obs} - |I_{calc}||/\sum I_{obs}$ and based on integrated reflection intensities, is shown in Fig. 1 as a function of *x*. A distinct R_I minimum, with minimum standard deviations of the parameters, was obtained for $x = 0\cdot07$, thus indicating a strong preference of Ni^{2+} for the *M*(2) sites. (The standard error of *x* is estimated to $\pm0\cdot01$ from Fig. 1 but is probably greater owing to the restrictions imposed upon the thermal parameters.) The final *R* values for the $x = 0\cdot07$ refinement were: $R_I = 0\cdot052$, $R_p = 0\cdot10$, $R_{wp} = 0\cdot13$ (*cf.* Rietveld, 1969). The atomic coordinates are given in Table 1. The observed and calculated intensity profile is shown in Fig. 2. The raw intensity data and the calculated and observed integrated intensities have been deposited.*

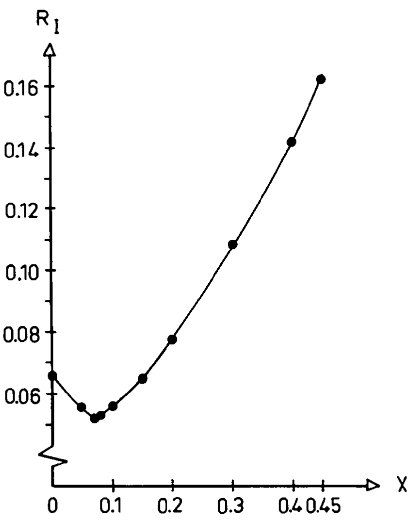

Fig. 1. The R_I values obtained from the Rietveld profile refinements *vs* *x* for the Ni-containing γ phase, expressed as γ-$(Zn_{1-x}Ni_x)_2^{M(1)}(Zn_{0\cdot1+2x}Ni_{0\cdot9-2x})^{M(2)}(PO_4)_2$, with $0 \le x \le 0\cdot45$.

Table 1. *Final atomic parameters* ($\times10^3$) *for* γ-$(Zn_{0\cdot70}Ni_{0\cdot30})_3(PO_4)_2$ *with e.s.d.'s in parentheses*

Space group $P2_1/n$, No. 14 $[\pm(x,y,z); \pm(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)]$. The isotropic overall temperature factor was refined to $B = 0\cdot2$ (1) Å^2.

	x	*y*	*z*
M(1)	617 (1)	144 (1)	96 (2)
M(2)	0	0	500
P	191 (2)	198 (2)	28 (2)
O(1)	42 (2)	138 (1)	829 (2)
O(2)	122 (2)	202 (1)	302 (2)
O(3)	258 (1)	363 (2)	947 (2)
O(4)	364 (2)	76 (2)	48 (2)

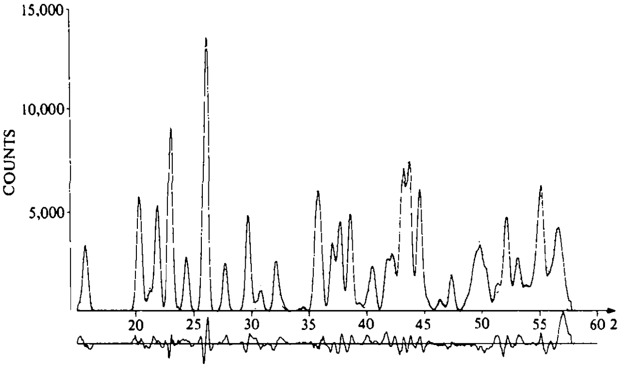

Fig. 2. The least-squares fit obtained between the observed intensities (continuous line) and calculated intensities (points) for γ-$(Zn_{0\cdot70}Ni_{0\cdot30})_3(PO_4)_2$ (neutron diffraction data). The discrepancy in the fit ($\Delta I = I_{obs} - I_{calc}$) is plotted below on the same scale.

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* Primary diffraction data and calculated and observed integrated intensities have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36050 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion

The structure of γ-$(\mathrm{Zn}_{0\cdot70}\mathrm{Ni}_{0\cdot30})_3(\mathrm{PO}_4)_2$ is built up of $M(1)\mathrm{O}_5$, $M(2)\mathrm{O}_6$, and PO_4 polyhedra. [Illustrations have been given by Calvo (1963) and Nord (1977)]. $M(1)\mathrm{O}_5$ is a distorted trigonal bipyramid and $M(2)\mathrm{O}_6$ a fairly regular octahedron with a center of symmetry. Zn concentrates strongly at the $M(1)$ and Ni at the $M(2)$ sites. Some interatomic distances and angles are summarized in Table 2, with corresponding values for γ-$(\mathrm{Zn}_{0\cdot97}\mathrm{Mn}_{0\cdot03})_3(\mathrm{PO}_4)_2$ (Calvo, 1973) added for comparison. The average P—O distance is 1·56 (2) Å which is slightly longer than normal; the M—O distances are quite reasonable. It is noteworthy that the mean $M(2)$—O has decreased in the Ni-containing γ phase whereas the mean $M(1)$—O is almost unchanged. This reflects the situation that the smaller Ni^{2+} ions preferentially occupy the $M(2)$ sites thereby decreasing the $M(2)$—O distances. The observed cation distribution may again explain the maximum solubility of Ni in the 'γ-$\mathrm{Zn}_3(\mathrm{PO}_4)_2$' structure which is about 33 at.% Ni; it seems that the γ structure tends to collapse when practically all $M(2)$ sites have been filled by Ni and only the 'less attractive' $M(1)$ sites are left. The same situation was also observed for the γ-$(\mathrm{Zn,Fe})_3(\mathrm{PO}_4)_2$ solid solutions (Annersten *et al.*, 1980). Accordingly, Ni^{2+} and Fe^{2+} here play the role of stabilizing cations in agreement with the theory proposed by Calvo (1963).

Table 2. *M—O distances* (Å) *and angles* (°)

The values for γ-$(\mathrm{Zn}_{0\cdot97}\mathrm{Mn}_{0\cdot03})_3(\mathrm{PO}_4)_2$ have been calculated from atomic parameters originating from an X-ray single-crystal structural study by Calvo (1973). All atoms are numbered as in Table 1.

	γ-$(\mathrm{Zn}_{0\cdot70}\mathrm{Ni}_{0\cdot30})_3$-$(\mathrm{PO}_4)_2$	γ-$(\mathrm{Zn}_{0\cdot97}\mathrm{Mn}_{0\cdot03})_3$-$(\mathrm{PO}_4)_2$
$M(1)$—O(1)	2·26 (2)	2·40 (1)
$M(1)$—O(2)	1·97 (2)	1·93 (1)
$M(1)$—O(3)	2·00 (1)	1·98 (1)
$M(1)$—O(4)	1·98 (2)	1·95 (1)
$M(1)$—O(4^{i})	1·98 (2)	2·01 (1)
$M(1)$—O mean	2·04 (2)	2·05 (1)
$M(2)$—O(1) (×2)	2·03 (1)	2·01 (1)
$M(2)$—O(2) (×2)	2·19 (1)	2·20 (1)
$M(2)$—O(3) (×2)	2·14 (1)	2·23 (1)
$M(2)$—O mean	2·12 (1)	2·15 (1)
O—$M(1)$—O range	72–165	67–164
O—$M(1)$—O mean	106	105
O—$M(2)$—O range*	83–97	82–98
O—$M(2)$—O mean*	90	90

Symmetry code: (i) $1-x, -y, -z$.

* The 180° angles are not included.

The intracrystalline Zn^{2+}/M^{2+} exchange in the γ-$(\mathrm{Zn},M)_3(\mathrm{PO}_4)_2$ orthophosphates may be expressed more explicitly by the distribution coefficient $K_D = X_{\mathrm{Zn}}[M(1)].X_M[M(2)]/X_{\mathrm{Zn}}[M(2)].X_M[M(1)]$. Thus a random distribution makes K_D equal to unity; the more M^{2+} orders onto the $M(2)$ sites, the greater is the K_D value. In the present Zn/Ni solid solution $K_D \simeq 40$. Corresponding K_D values, around 1100 K, have earlier been determined for γ-$\mathrm{Zn}_2\mathrm{Mg}(\mathrm{PO}_4)_2$ (Nord, 1977) and some γ-$(\mathrm{Zn,Fe})_3(\mathrm{PO}_4)_2$ compounds (Annersten *et al.*, 1980); these K_D values were in the region 20–30. It is evident that Zn always has the strongest affinity for the $M(1)$ sites, while Ni rather than Mg or Fe seems to have the strongest preference for the $M(2)$ sites. As regards Ni^{2+}, its readiness for octahedral coordination is well established and may be explained by the large crystal-field stabilization energy (*e.g.* Burns, 1970). The present study, though, indicates that a minor part of the Ni^{2+} ions do reside in five-coordinated sites. Although rare, five-coordinated Ni^{2+} has also been reported in a few other oxosalt structures such as α-$\mathrm{Ni}_2\mathrm{P}_2\mathrm{O}_7$ (Lukaszewicz, 1967) and $\mathrm{Ni}_2(\mathrm{PO}_4)\mathrm{F}$ (Auh & Hummel, 1974). Further cation-distribution studies involving Zn and Ni are in progress.

Professors Arne Magnéli and Peder Kierkegaard (Arrhenius Laboratory) are cordially thanked for valuable discussions and comments regarding this work. We are also greatly indebted to Dr Roland Tellgren (University of Uppsala) for his willing help during the collection of the neutron diffraction data. This work has received financial support from the Swedish Natural Science Research Council.

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