Structure Refinements of $Co_3(PO_4)_2$. A Note on the Reliability of Powder Diffraction Studies

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The crystal structure of $Co_3(PO_4)_2$ ($P2_1/n$) has been refined by means of the Rietveld full-profile technique, based on powder diffraction data. Photographic X-ray data (Guinier-Hägg) as well as neutron powder diffractometer data have been used. These results and an earlier rigid-group structural refinement with Guinier-Hägg data (Nord, 1974) agree with an X-ray single-crystal study of $Co_3(PO_4)_2$ (Anderson, Kostiner, Miller and Rea, 1975), although individual $Co-O$ and $P-O$ bond distances may deviate by $1-2\ \sigma$. The average distances within each polyhedron agree still better. Other examples from the literature are given, and the usefulness of powder diffraction data is discussed.

When X-ray crystallography was in its infancy, powder diffraction data were used for most structure determinations, but since about 1930 single-crystal data have mostly been utilized for this purpose. However, powder diffraction techniques have gained renewed importance, principally owing to the development of the ingenious full-profile refinement technique by Rietveld.[1] This method was first used for neutron diffraction data, but has later been extended to X-ray powder patterns recorded by Guinier-Hägg focusing cameras[2-4] or powder diffractometers.[5,6] Young[7] predicted that papers on X-ray powder diffraction soon may outnumber those on neutron powder diffraction.

At the XII International Congress of Crystallography in Ottawa, 1981, Langford[8] read a review paper on the Rietveld technique, entitled "The renaissance of powder diffraction: from ugly duckling to beautiful swan". It was met with applause but also some criticism. One of the critics started by saying that "he wanted to pour some cold water down the neck of the beautiful swan". The reliability of the profile-fitting technique has also been questioned by Sakata and Cooper[9] and some other authors.

Within a research project on solid solutions, we have frequently based our studies on the $Mg_3(PO_4)_2$ and $Co_3(PO_4)_2$ structures (e.g. Refs. 10, 11). X-Ray powder diffraction data were used by Nord[12] to show that $Co_3(PO_4)_2$ is isostructural with magnesium orthophosphate.[13] A detailed structural investigation confirming this fact appeared shortly afterwards.[14] We now report on three Rietveld full-profile refinements of $Co_3(PO_4)_2$, one based on neutron data and two on photographic (Guinier-Hägg) X-ray powder diffraction data. The results of the various refinement techniques are compared, and a brief discussion on the reliability of powder diffraction data and the Rietveld technique is given, together with other examples from the literature.

EXPERIMENTAL

Two samples, A and B (each~5 g $Co_3(PO_4)_2$), were prepared as earlier described.[12] Accurate X-ray powder diffraction data were obtained with an XDC-700 Guinier-Hägg type focusing camera ($CrK\alpha_1$ radiation, $\lambda=2.28975$ Å, $r=50.00$ mm; KCl internal standard). Copper radiation was not used because of the strong X-ray fluorescence from cobalt. The photographs were evaluated with a computer-controlled film scanner and

Table 1. Fractional atomic coordinates and isotropic temperature factors ($Å^2$) for the three profile-refinements of $Co_3(PO_4)_2$. Space group $P2_1/n$ (No. 14, non-standard setting) with general positions 4(*e*): $\pm(x,y,z)$; $\pm(1/2-x, 1/2+y, 1/2-z)$.

Atom	Parameter	Neutron data (study II)	Guinier-Hägg photographic X-ray data Sample *A* (III)	Sample *B* (IV)
Co(1)	x	0.609(3)	0.615(1)	0.615(1)
	y	0.137(3)	0.142(1)	0.142(1)
	z	0.076(3)	0.096(1)	0.097(1)
Co(2)	x	0	0	0
	y	0	0	0
	z	1/2	1/2	1/2
P	x	0.198(1)	0.196(1)	0.205(1)
	y	0.190(1)	0.193(1)	0.192(1)
	z	0.033(2)	0.034(2)	0.037(2)
O(1)	x	0.052(1)	0.053(2)	0.048(2)
	y	0.144(1)	0.148(2)	0.145(2)
	z	0.826(2)	0.831(3)	0.838(4)
O(2)	x	0.128(1)	0.128(2)	0.121(2)
	y	0.199(1)	0.202(2)	0.199(2)
	z	0.306(2)	0.310(3)	0.306(3)
O(3)	x	0.253(1)	0.258(2)	0.257(2)
	y	0.363(1)	0.371(2)	0.370(2)
	z	0.950(1)	0.947(3)	0.954(3)
O(4)	x	0.355(1)	0.362(2)	0.367(3)
	y	0.078(1)	0.089(3)	0.085(2)
	z	0.053(2)	0.051(3)	0.050(3)
Co	$B(Co)$	0.8(4)	0.0(2)	−0.6(3)
P	$B(P)$	0.4(2)	−0.4(3)	−1.3(4)
O	$B(O)$	0.1(1)	−0.8(3)	−1.7(3)

associated programs.[15] The transmission intensities were measured up to $\theta \approx 44°$, giving about 2500 recorded intensity values for each photograph after exclusion of three internal standard (KCl) reflections, comprising 74 independent, partly overlapping Bragg reflections. The step length (in θ) is 0.0127°; the peak half-widths are around 0.1° (in θ) so that each reflection peak comprises 12−25 individual intensity values. The background values were subtracted, and the net intensities corrected for polarization and Lorentz effects.[2] Both samples were found to be very pure. Unit cell parameters were refined with the program PIRUM;[16] they are (average of *A* and *B*): a=7.556(1), b=8.371(2), c=5.064(1) Å, β=94.05(1)°, V=319.5(1) $Å^3$ ($P2_1/n$ symmetry; Z=2). The calculated density is 3.812 g cm^{-3}.

Neutron powder diffraction data were collected with an OPUS-3 diffractometer, equipped with five ^{3}He detectors, at the 2 MW JEEP-2 reactor at Kjeller, Norway. The sample (a mixture of *A* and *B* amounting to about 10 g) was kept in a thin-walled vanadium cylinder. Accurate powder data were collected for $5 \le \theta \le 45°$

($\Delta\theta$=0.025°, $\lambda \approx 1.8820$ Å), with a total scan time of 4 days. The intensity profile contained 144 independent reflections. The graphically determined background was subtracted from the intensity profile to give net intensities.

THE PROFILE REFINEMENTS

The neutron powder diffraction data were processed with Rietveld's full-profile refinement procedure.[1] Some trial refinements were first made to settle the average wavelength, scale factor, zero point, *etc.* In the final stages, the complete structure was refined with 25 parameters: one scale factor, 18 atomic positional parameters, three isotropic temperature factors (for cobalt, phosphorus, and oxygen) and three "profile" parameters. The latter define the almost perfectly symmetric Gaussian shape of the peak profiles. The θ-dependence of H_k, the full width at half maximum of the peak (with maximum at $\theta=\theta_k$), is defined by

$H_k{}^2 = U \tan^2\theta_k + V \tan\theta_k + W$ (cf. Ref. 17).

The scattering amplitudes were taken from the *International Tables for X-Ray Crystallography*.[18] The final R values[1] were $R_I = 0.067$ and $R_p = 0.11$. The atomic parameters are listed in Table 1. Due to the comparatively small scattering amplitude of cobalt, the Co atoms have acquired larger e.s.d. values than the other atoms.

The A and B samples of $Co_3(PO_4)_2$ were then structurally refined with a Guinier-Hägg X-ray version of Rietveld's program, developed by Malmros and Thomas[2] and later modified by Werner *et al.*[3,4] The parameters to be refined were equivalent to those of the neutron diffraction study, with exception of the profile parameters. Sonneveld and Visser[19] found that the modified Lorentzian function (henceforward: *ML*) defining the peak profiles performed better with Guinier data than did either the Gaussian or the Lorentzian function. This was later confirmed for Guinier-Hägg data by Malmros and Thomas.[2] However, an empirical asymmetry parameter *P* was also introduced,[2] thus increasing the number of parameters by one with respect to the neutron refinement, to 26 instead of 25. The refinements were successfully carried out, arriving at $R_F = 0.090$ (for A) and $R_F = 0.097$ (for B). The atomic parameters are listed in Table 1. The negative "temperature" factors are probably due to absorption effects (cf. Refs. 3, 20). The standard deviations of the refined parameters have been obtained by use of all observed intensity values for the peaks (cf. Ref. 21). The samples A and B have been checked with a JEOL JSM-35 scanning electron microscope showing that there is no reason to expect preferred orientation effects.

Tables of observed and calculated values of the integrated reflections for the three profile refine-

Table 2. Some crucial data characterizing the five structure refinements of $Co_3(PO_4)_2$.

Study No.	I	II	III	IV	V
Technique	single-crystal refinement	Rietveld refinement (A+B)	Rietveld refinement (A)	Rietveld refinement (B)	Rigid-group least-squares refinement
Reference	Anderson *et al.*[14]	This work	This work	This work	Nord[12]
Data	X-ray single-crystal diffractometer	Neutron powder diffractometer	Guinier-Hägg (X-ray)	Guinier-Hägg (X-ray)	Guinier-Hägg (X-ray)
Radiation	$MoK\alpha$	Neutrons	$CrK\alpha_1$	$CrK\alpha_1$	$FeK\alpha_1$
Wavelength (Å)	0.71069	1.8820	2.28975	2.28975	1.9360
Number of reflections	1032	144	74	74	55
Absorption correction	yes	no (negligible)	no	no	no
Number of refined parameters	59	25	26	26	10
Temperature factors	anisotropic	isotropic (three)	isotropic (three)	isotropic (three)	isotropic overall temp. factor (constrained)
R_F	0.039	0.067^a	0.090	0.097	0.14

^{a} Note: R_I is given for refinement (II).

Table 3. Interatomic distances (Å), with observed standard deviations, for the five refinements of $Co_3(PO_4)_2$. D=distance, Δ=the difference (Å) between the value in question and the corresponding value from (I).

	Study I Anderson et al.[14] X-ray single-crystal data	Study II This work. Neutron profile refinement		Study III This work. X-ray profile refinement		Study IV This work. X-ray profile refinement		Study V Nord.[12] Rigid-group least-squares refinement (X-ray)	
	D	D	Δ	D	Δ	D	Δ	D	Δ
Co(1)–O(1)	2.229(3)	2.28(2)	0.05	2.19(2)	−0.04	2.23(2)	0.00	2.38(5)	0.15
Co(1)–O(2)	1.978(3)	1.95(2)	−0.03	1.95(1)	−0.03	1.99(1)	0.01	1.94(5)	−0.04
Co(1)–O(3)	2.109(3)	2.12(2)	0.01	2.03(2)	−0.08	2.04(2)	−0.07	2.05(5)	−0.06
Co(1)–O(4)	1.988(3)	1.95(2)	−0.04	1.96(1)	−0.03	1.96(1)	−0.03	2.01(5)	0.02
Co(1)–O(4')	2.012(3)	1.98(2)	−0.03	2.08(2)	0.07	2.05(2)	0.04	2.02(5)	0.01
Average	2.063	2.056	−0.007	2.042	−0.021	2.054	−0.009	2.080	0.017
Co(2)–O(1) (×2)	2.058(3)	2.06(2)	0.00	2.10(2)	0.04	2.10(2)	0.04	2.02(5)	−0.04
Co(2)–O(2) (×2)	2.144(3)	2.18(2)	0.04	2.19(2)	0.05	2.18(2)	0.04	2.16(5)	0.02
Co(2)–O(3) (×2)	2.174(3)	2.18(2)	0.01	2.12(1)	−0.05	2.14(1)	−0.03	2.21(5)	0.04
Average	2.125	2.140	0.015	2.137	0.012	2.140	0.015	2.130	0.005
P–O(1)	1.526(3)	1.52(1)	−0.01	1.49(2)	−0.04	1.54(2)	0.01	1.53^a	0.00
P–O(2)	1.533(3)	1.52(1)	−0.01	1.53(2)	0.00	1.53(2)	0.00	1.53^a	0.00
P–O(3)	1.554(3)	1.58(1)	0.03	1.61(2)	0.06	1.60(2)	0.05	1.53^a	−0.02
P–O(4)	1.540(3)	1.51(1)	−0.03	1.52(2)	−0.02	1.50(2)	−0.04	1.53^a	−0.01
Average	1.538	1.533	−0.005	1.537	−0.001	1.542	0.004	1.530^a	−0.008
O–P–O range (°)	104.6–112.9	104.2–114.6		104.6–117.0		104.7–117.1		109.5^a	

^{a} Constrained value.

ments can be obtained from the authors on request. Illustrations of the crystal structure have been published earlier.[13,14]

DISCUSSION

In addition to the three profile-refinements described above, our comparison will include the earlier mentioned studies by Nord[12] and by Anderson et al.[14] The former study was based on Guinier-Hägg photographic data (Fe$K\alpha_1$ radiation), using 55 integrated intensities from well-resolved reflections. The structure was refined utilizing the rigid-group least-squares program system of Scheringer,[22] by which the number of parameters was reduced to 10 by assuming PO_4 to be a rigid, regular tetrahedron. The study by Anderson et al.[14] was based on single-crystal diffractometer data (Mo$K\alpha$ radiation). Some crucial data characterizing the five refinements (numbered I–V) are given in Table 2.

In our comparison we will primarily discuss interatomic distances, since these are more relevant and more easily compared than a set of atomic coordinates (see Table 3). All atoms are denoted in accordance with the first study of $Co_3(PO_4)_2$.[12] The bond length values from the single-crystal study[14] (No. I) are regarded as "correct". All distance differences, called Δ, between (I) and refinements (II)–(V) are included in Table 3. We will first compare the average distances within the polyhedra (CoO_5, CoO_6 and PO_4) which build up a three-dimensional framework forming the $Co_3(PO_4)_2$ structure. For refinements (II)–(V) these values agree fairly well with the "correct" values; the differences are in the range 0.001–0.021 Å ($\leq 1\sigma$). The O–P–O angles are also fairly similar for all refinements.

Among the individual bond length values, the largest differences (i.e., Δ values) are found in the distorted trigonal bipyramid $Co(1)O_5$. However, Co(1)–O(1) always shows up as the largest bond distance, while the shortest distance is Co(1)–O(2) in all studies except (IV). In study (V), Co(1)–O(1) is considerably longer (2.38 Å) than in the four other refinements. The fairly regular $Co(2)O_6$ octahedron and the almost regular PO_4 tetrahedron exhibit less scattering of bond distance values than the $Co(1)O_5$ group.

In this comparison of structure refinements, the neutron diffraction study (No. II) comes out

as the second best. (No. I is naturally the best one). This is partly due to a larger number of observed reflections, but we also attribute the good result of the neutron refinement to a better defined peak-shape function (see below). The Δ differences for (II) are in the range 0.00–0.05 Å for the individual distances. The largest Δ values are registered in the cobalt–oxygen polyhedra [e.g. Co(1)–O(1) with Δ=0.05 Å], probably due to the small scattering amplitude of cobalt which reduces the accuracy in the respective positional parameters. The "Guinier-Hägg" X-ray refinements (III and IV) gave somewhat larger Δ values and standard deviations than (II). It is interesting to note, though, that the results of (III) and (IV) closely resemble each other, thus indicating good reproducibility for this method (for instance, compare the Co(1)–O(3) and the P–O(3) D and Δ values in Table 3). Moreover, it should be emphasized that refinements (III) and (IV) certainly do not exaggerate the usefulness of the profile-refinement method; the long wavelength used (Cr$K\alpha_1$) is not advantageous since it considerably reduces the number of observed reflections: the 26 parameters were refined on the basis of only 74 reflections. (The use of Cu$K\alpha_1$ radiation usually improves the accuracy, as will be exemplified below). Refinement (V) is the "loser" in Table 3, although it is surprisingly good since only 55 reflections were used and many structural parameters were constrained.

An extensive review of Rietveld refinements with neutron powder diffraction data has been published by Cheetham and Taylor.[23]

In a recent study of forsterite, Mg_2SiO_4, Lager et al.[24] have obtained excellent agreement between structural parameters from single-crystal diffractometer data and from a Rietveld refinement based on neutron powder diffraction data (464 reflections, 47 parameters) collected with the high-resolution time-of-flight powder diffractometer at Argonne National Laboratory's ZING-P pulsed neutron source. It thus seems that very good results can be achieved with the Rietveld technique, applied on a simple crystal structure, provided the data are first-class.

Among the critics of the Rietveld technique, Sakata and Cooper[9] claim that the standard deviations of the structural parameters are determined incorrectly and underestimated by a factor of at least two. Judging from our results obtained

for $Co_3(PO_4)_2$, this is not true for the neutron diffraction study (No. II). Albinati and Willis,[25] Prince[26] and many others have also shown that the fears of Sakata and Cooper are exaggerated.

As regards the applicability of the Rietveld method on X-ray diffraction data, a cumbersome complication arises because of the difficulty to define the peak profiles accurately.[27] For geometrical reasons this problem is still more complicated with Guinier-Hägg data than for powder diffractometer data, since there are to some extent individual variations of profiles, i.e. the peak-shape is not only dependent on tan θ (cf. Ref. 28). However, many good results have been obtained with Rietveld refinements based on Guinier-Hägg X-ray data by use of the *ML* peak-shape function. Some examples, all with $CuK\alpha_1$ data (which is more favourable than $CrK\alpha_1$) will be quoted.

Malmros and Thomas[2] obtained good agreement between refinements of α-Bi_2O_3 with the Rietveld technique and with X-ray single-crystal data. Further early examples of successful full-profile refinements are the studies of $Mg_3Nb_6O_{11}$[29] and $Zn_2Mg(PO_4)_2$.[30] The structure of $Ni_3(PO_4)_2$ has recently been profile-refined from Guinier-Hägg data.[31] In spite of the disadvantage of a monoclinic angle of 91.12°, which implies severe overlap among reflections like *hkl* and *hkl̄*, all observed individual Ni—O and P—O distances were usually within ±0.02 Å of the "correct" values yielded by an earlier single-crystal study.[32]

To sum up, a structural study based on powder diffraction data is probably always inferior to one utilizing good single-crystal data. However, it is much easier to obtain a powder sample than a single crystal. With powder data, problems like twinning, absorption, or extinction may often be neglected. The Rietveld technique is certainly suitable for refinements of already known and comparatively simple crystal structures. However, the solution of moderately complex crystal structures solely from powder diffraction data is another important advantage of the Rietveld technique.[33-35] Many cation distribution studies have also been performed utilizing X-ray powder data (cf. Refs. 10,30,31). We therefore conclude that structural studies based on powder diffraction data may be very fruitful, especially when combined with the Rietveld full-profile refinement technique, and that there is no reason for the "ugly duckling" to hide among the reeds.

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