Short Communication

Single Crystal Study of $Mn_{0.8}Co_{0.2}P$

Helmer Fjellvåg[a] and Arne Kjekshus[b,*]

[a]Institute for Energy Technology, N-2007 Kjeller and [b]Department of Chemistry, University of Oslo, Blindern, N-0315 Oslo 3, Norway

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MnP is the prototype of an appreciable class of isostructural phases,[1] and many of the binary representatives have been characterized structurally by single crystal X-ray diffraction methods.[1] Information on the crystal structures of the ternary (solid solution) phases, on the other hand, has hitherto originated almost solely from powder diffraction measurements, mainly through Rietveld analyses of powder neutron diffraction data. A series of papers[2–5] in the early 1970's attempted to document that (binary) phases with the MnP-type structure have $Pn2_1a$ rather than *Pnma* space group symmetry. However, it was soon demonstrated[6] that this was a hasty and false conclusion based on inappropriate corrections for absorption and extinction, and that space group *Pnma* most probably applies to the entire MnP-type family.

In this work, single crystals of $Mn_{0.8}Co_{0.2}P$ were studied by X-ray diffraction in order to:

(*i*) check the reliability of the results[6] obtained by Rietveld analysis of powder neutron diffraction data for a sample with the same composition,

(*ii*) test whether the mirror-plane characteristic of space group *Pnma* is also present in ternary MnP-type phases, and

(*iii*) ascertain whether Mn and Co really are randomly distributed over the metal sub-lattice, considering *inter alia* the possibility of a split-model description for the metal atoms.

Experimental

Polycrystalline samples of $Mn_{1-t}Co_tP$ ($0.00 < t < 0.30$) were synthesized for MnP and CoP as described in Ref. 6. Single crystals (max. size $1\times1\times1$ mm; regular or needle shape) were obtained using tin-flux as a medium for crystal growth. The molar ratio $Mn_{1-t}Co_tP$: Sn was approx. 1 : 10, and the temperature was slowly reduced from 1050 to 800 °C over a period of 10 d. Single crystals were obtained in this manner for $0.00 \leqq t \leqq 0.2$. The compositions of the crystals thus obtained were checked by powder (crushed crystals, Guinier technique, Cu$K\alpha_1$ radiation, Si as internal standard) and single crystal X-ray methods, and further confirmed by microprobe analyses. The "analytical" control figures match the nominal t values quite well (within $\Delta t = \pm 0.02$). The microprobe analyses furthermore revealed that there is no significant contamination by Sn in the $Mn_{1-t}Co_tP$ crystals.

Single crystal X-ray data for $Mn_{0.8}Co_{0.2}P$ were collected on a $P\bar{1}$ four-circle diffractometer at the Max-Planck-Institut für Festkörperforschung, Stuttgart, using Mo$K\alpha_1$ radiation (λ = 71.069 pm; crystal size $0.2\times0.2\times0.2$ mm). 283 of 298 reflections were classified as observed in the structure refinement procedure. Empirical absorption corrections were made using 396 independent measurements on 11 different reflections recorded in the ψ-scan mode. Data reduction and refinement were performed according to the SHELXTL programme.[7] Isotropic extinction corrections were used.

A similar set of data (350 reflections) was col-

*To whom correspondence should be addressed.

lected for a single crystal of MnP, and subsequently treated by a corresponding data reduction and refinement procedure. The randomization of Mn and Co on the metal sub-lattice was simulated by coupling their positional as well as thermal parameters.

Results and discussion

The least-squares refined unit cell dimensions of the single crystal specimen studied (the nominal composition of the sample was $Mn_{0.80}Co_{0.20}P$ prior to the tin-flux treatment) are given in Table 1. Judged from the unit cell dimensions versus t relationships presented in Ref. 6, these dimensions correspond to $t = 0.18 \pm 0.01$ for $Mn_{1-t}Co_tP$, and the formula $Mn_{0.8}Co_{0.2}P$ is therefore used throughout the rest of this paper.

The crystal structure refinement for $Mn_{0.8}Co_{0.2}P$ was first performed assuming space group *Pnma*. The Mn, Co atoms were assumed to be randomly distributed over one 4*c* position, and the P atoms to occupy another 4*c* position. The final positional parameters are listed in Table 1 [thermal parameters (in pm^2): $U_{11} = 173(5)$, $U_{22} = 196(6)$, $U_{33} = 176(5)$ and $U_{13} = 0(2)$ for Mn, Co, and $U_{11} = 179(7)$, $U_{22} = 165(6)$, $U_{33} = 171(7)$ and $U_{13} = 11(4)$ for P; in all 14 variables, $R = 0.049$, GOOF = 1.42]. Refinement cycles in which the relative proportions of Mn and Co were allowed to vary indicated the composition $Mn_{0.78 \pm 0.02}Co_{0.22 \mp 0.02}P$, which agrees well with the microprobe analysis results (as well as with the t-value estimated from the unit cell dimensions, *vide supra*). The positional parameters given in Table 1 comply, within one or two standard deviations, with those derived from powder neutron diffraction data [$x_{Mn,Co} = 0.0061(21)$, $z_{Mn,Co} = 0.1940(20)$, $x_P = 0.1903(10)$ and $z_P = 0.5699(9)$ for $t = 0.20$][6].

Refinement for $Mn_{0.8}Co_{0.2}P$ was also carried out assuming space group $Pn2_1a$, but no significant improvement in the R-factor was obtained. Hence, the mirror-plane characteristic of space group *Pnma* is present in the crystal structure of $Mn_{0.8}Co_{0.2}P$. Generalizing this result, there appears to be no distinction between the binary and ternary MnP-type phases in this respect.

In order to test the possibility of a split-model for Mn and Co in $Mn_{0.8}Co_{0.2}P$, viz. allowing for a degree of bonding distinction between the two kinds of metal atoms, two sets of 4*c* positions were introduced in the refinement. There were, in fact, some indications in difference Fourier maps that this might be appropriate. However, the introduction of these additional degrees of freedom in the structure did not lead to improvements in the R-factor. The conclusion is, accordingly, that the assumption of long-range, random distribution of Mn and Co over one metal sublattice is a good approximation.

It is natural to compare the results for $Mn_{0.8}Co_{0.2}P$ with those obtained in the parallel study of MnP. The structural reexamination of MnP single crystals gave the unit cell dimensions and positional parameters listed in Table 1. These findings are in excellent agreement with those obtained by powder neutron diffraction,[6] as well as with the earlier single crystal X-ray diffraction results.[8] The shifts in the positional parameters on going from MnP to $Mn_{0.8}Co_{0.2}P$ are significant (3–10 standard deviations) but numerically quite small, and the main structural changes are that the two shortest metal–metal distances become slightly contracted, viz. from 270.5 and 281.7 pm for $t = 0.00$ to 270.1 and 277.8 pm for $t = 0.2$. Small changes are also found for the metal–P bonds, e.g. the average bond distance within the distorted (Mn,Co)P_6 octahedron is reduced from 235.8 pm in MnP to 234.8 pm in $Mn_{0.8}Co_{0.2}P$.

Table 1. Unit cell dimensions and positional parameters (with standard deviations) for $Mn_{1-t}Co_tP$ with $t = 0.00$ and 0.2 as derived by X-ray diffraction of single crystals (space group *Pnma*, all atoms in 4*c* positions).

t	a/pm	b/pm	c/pm	Atom	x	z
0.00	525.9(1)	317.3(1)	592.0(1)	Mn	0.00470(2)	0.19651(2)
				P	0.18784(5)	0.56855(5)
0.2	523.9(2)	316.3(2)	588.5(2)	Mn,Co	0.0037(1)	0.1979(1)
				P	0.1887(3)	0.5690(2)

These changes are also reflected in the contraction of the unit cell volume of $Mn_{1-t}Co_tP$ with increasing t reported in Ref. 6.

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