

Rietveld Refinements of Four $(\text{Zn,Mg})_3(\text{PO}_4)_2$ Solid Solutions

PATRICIA BÉNARD

*Laboratoire de Cristallochimie (LA 254), Université de Rennes 1,
Avenue du Général Leclerc, F-35042 Rennes Cedex, France*

AND ANDERS G. NORD, PER-ERIK WERNER,*
AND MARIANNE WESTDAHL

*Department of Structural Chemistry, Arrhenius Laboratory,
University of Stockholm, S-10691 Stockholm, Sweden*

Received October 11, 1991; in revised form February 4, 1992; accepted February 6, 1992

Four $(\text{Zn}_{1-x}\text{Mg}_x)_3(\text{PO}_4)_2$ solid solutions have been prepared at 800°C and the crystal structures ($P2_1/n$; $Z = 2$) refined with the Rietveld technique on the basis of X-ray powder diffractometer data. The structure factor R -values are in the region 0.03–0.08 for 274 independent reflections. The $\text{Zn}^{+2}/\text{Mg}^{+2}$ cation distribution is ordered with zinc preferably at the five-coordinated and magnesium at the six-coordinated metal sites. The cation distribution coefficient K_D is around 20 irrespective of the composition. © 1992 Academic Press, Inc.

Introduction

The distribution of divalent-metal cations between five- and/or six-coordinated sites has for many years been studied at this Institute by diffraction techniques or Mössbauer spectroscopy (e.g. Ref. (1)). The first results were published in 1977 by Nord (2). Guinier X-ray data and Rietveld refinements (3) had been used to study the solid solution $\text{Zn}_2\text{Mg}(\text{PO}_4)_2$ ($P2_1/n$) with one distinct five-coordinated and one six-coordinated metal site. The cations were strongly ordered with zinc preferably at the five-coordinated sites and with a cation distribution coefficient $K_D \cong 20$ for samples quenched from 1050°C. Later studies of 22 $(\text{Zn}_{1-x}\text{Mg}_x)_3(\text{PO}_4)_2$ solid

solutions prepared at 800°C showed some slight deviations from Vegard's law (4). Furthermore, another investigation by means of ^{31}P magic angle spinning NMR of $(\text{Zn}_{1-x}\text{Mg}_x)_3(\text{PO}_4)_2$ phases, prepared and quenched from 1000°C, displayed an anomalously large spread among the cation distribution coefficients, K_D with values ranging from 3 to 290 (5). For these reasons we have now undertaken further studies of four $(\text{Zn,Mg})_3(\text{PO}_4)_2$ compositions. An illustration of the structure is shown in Fig. 1.

Experimental

The preparation methods have been described earlier (2, 4). The four samples were quenched from 800°C in cool water. All samples were analyzed with a JEOL JSM-840

* To whom correspondence should be addressed.

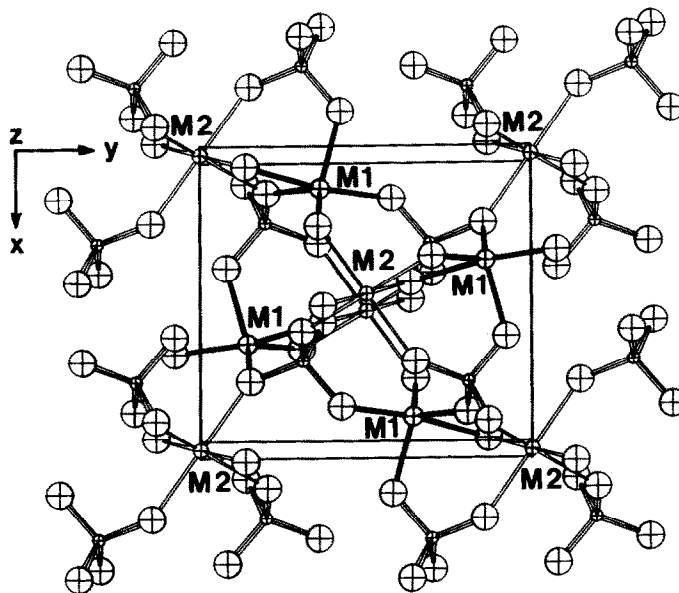


FIG. 1. The crystal structure of $\gamma\text{-(Zn,Mg)}_3(\text{PO}_4)_2$ viewed down the c -axis.

scanning electron microscope equipped with a LINK system for energy-dispersive micro-X-ray analysis. Accurate X-ray powder diffraction data of each compound were collected at 295 K with a STOE STADI/P powder diffractometer, using a sample mounted in a 0.3-mm rotating capillary. A symmetric focusing germanium crystal monochromator (focal distance = 440 mm) was used to give $\text{CuK}\alpha_1$ radiation. The diffraction data were collected with a small linear position sensitive detector (PSD) covering 7.0° in 2θ . The PSD was moved in steps of 0.2° , thus giving an average intensity of 35 measurements at each 2θ position ($19^\circ \leq 2\theta \leq 91^\circ$).

In addition, Guinier-Hagg data ($\text{CuK}\alpha_1$) with silicon ($a = 5.430880 \text{ \AA}$ at 25°C (6)) as internal standard were also collected and used for refinement of the unit cell dimensions (7), cf. results in Table I. Each cell dimension changes in an almost linear way with the composition. The figures of merit given, $M(20)$ and $F(20)$, have been defined by de Wolff (8) and Smith and

Snyder (9). The samples were found to be very pure, with all reflections indexed except in $(\text{Zn}_{0.5}\text{Mg}_{0.5})_3(\text{PO}_4)_2$ (one very weak unindexed line at 2.9341 \AA) and $(\text{Zn}_{0.2}\text{Mg}_{0.8})_3(\text{PO}_4)_2$ (impurity line at 2.9633 \AA).

Whenever applicable, data for the pure end member $\text{Mg}_3(\text{PO}_4)_2$ (10) are added for comparison. However, pure $\gamma\text{-Zn}_3(\text{PO}_4)_2$ does not exist, and the only single-crystal study of an Mn-doped $\gamma\text{-Zn}_3(\text{PO}_4)_2$ phase suffers from uncertainty regarding chemical composition and crystallographic accuracy (11). Accordingly, no data for the other end member of the (Zn,Mg) series can be given.

Structure Refinements

Rietveld (3) full-profile refinements were performed with the program DBW3.2S by Wiles, Sakthivel, and Young (12), implemented on a CONVEX 220 computer by one of us (P.-E.W). The atomic coordinates of $\text{Zn}_2\text{Mg}(\text{PO}_4)_2$ (2) were used as starting parameters. In the final refinements the follow-

TABLE I
UNIT CELL DIMENSIONS OF FOUR $(Zn_{1-x}Mg_x)_3(PO_4)_2$ SOLID SOLUTIONS

	$Zn_{73}Mg_{27}$	$Zn_{50}Mg_{50}$	$Zn_{40}Mg_{60}$	$Zn_{20}Mg_{80}$	Mg_{100}^a
$a(\text{Å})$	7.5601(4)	7.5727(4)	7.5794(6)	7.5913(9)	7.5957(8)
$b(\text{Å})$	8.3585(5)	8.3109(5)	8.2881(7)	8.2514(8)	8.2305(5)
$c(\text{Å})$	5.0529(4)	5.0613(3)	5.0661(4)	5.0726(5)	5.0775(5)
$\beta(^{\circ})$	95.001(4)	94.767(4)	94.579(6)	94.291(8)	94.05(1)
$V(\text{Å}^3)$	318.08(4)	317.44(4)	317.23(6)	316.85(8)	316.6(1)
$M(2\theta)$	107	82	50	48	
$F(2\theta)$	156(0.005,27)	117(0.006,28)	69(0.006,47)	59(0.011,29)	

Note. $M(2\theta)$ and $F(2\theta)$ are figures of merit as defined in Refs. (8) and (9). $Zn_{73}Mg_{27}$ stands for $(Zn_{0.73}Mg_{0.27})_3(PO_4)_2$, and so on.

^a Data for $\gamma\text{-Mg}_3(\text{PO}_4)_2$ from Ref. (10).

ing parameters were refined: one scale factor, two mixing parameters to define a theta-dependent pseudo-Voigt profile shape function, three peak half-width parameters (U , V , W), zero point, one asymmetry param-

eter, six parameters in a polynomial describing the background, four unit cell parameters, 19 structural parameters describing the atomic positions and metal occupancies, and three isotropic temperature factors (for

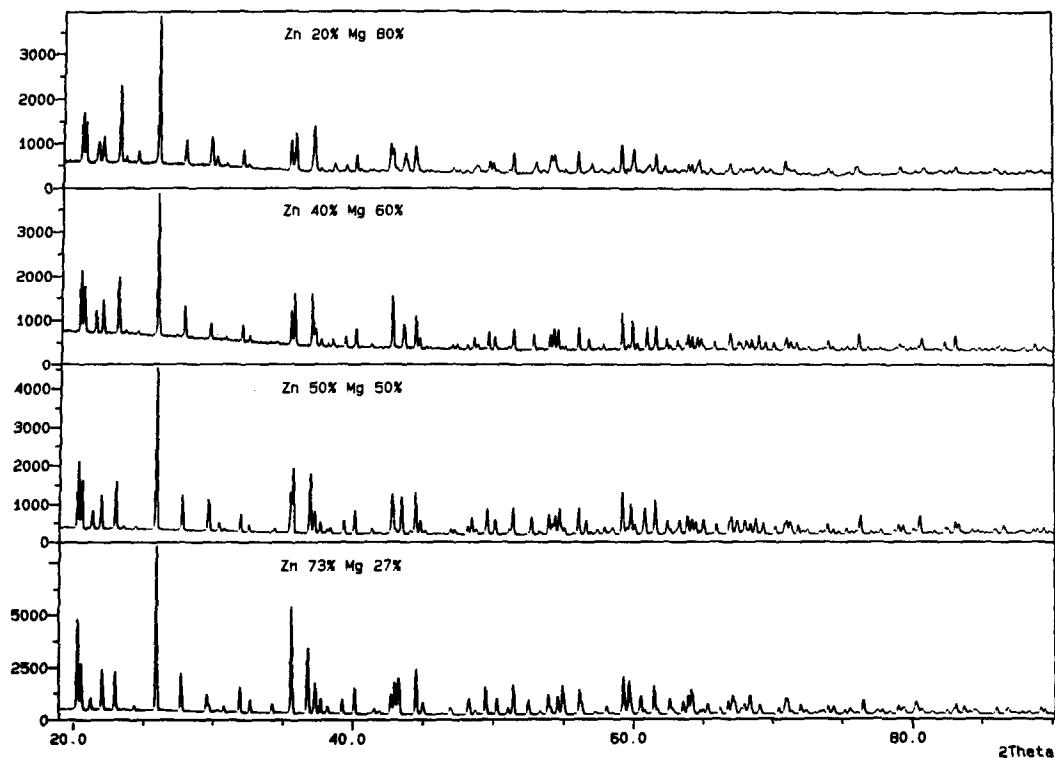


FIG. 2. Observed diffraction patterns for $(Zn_{1-x}Mg_x)_3(PO_4)_2$ solid solutions.

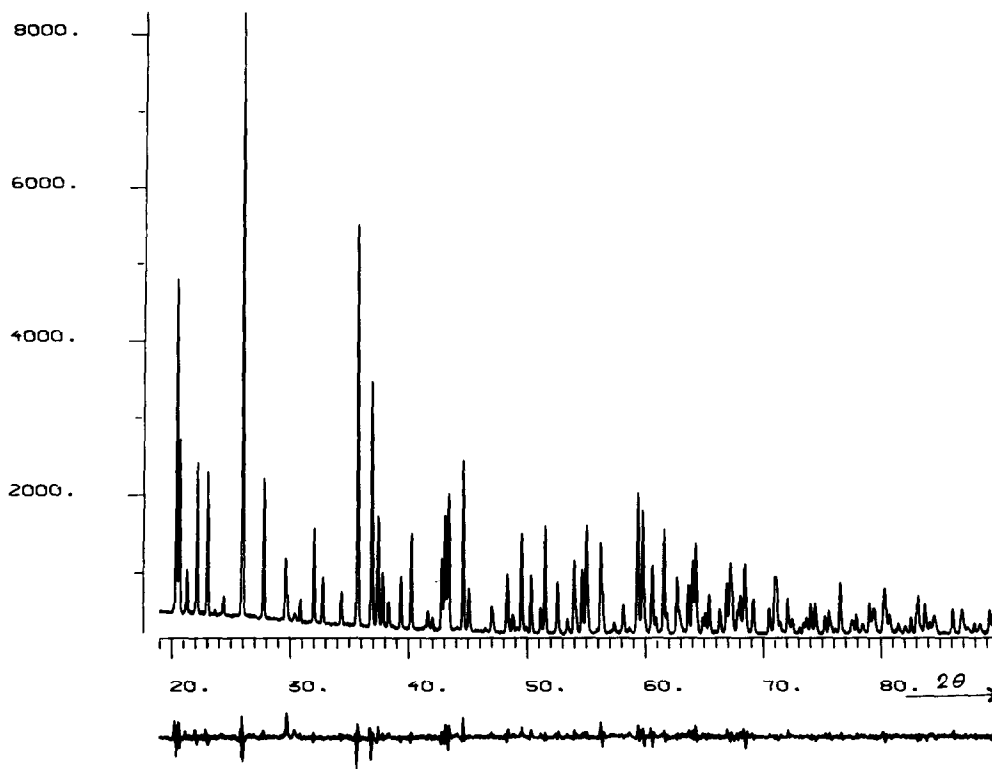


FIG. 3. Final Rietveld plot for $(\text{Zn}_{0.73}\text{Mg}_{0.27})_3(\text{PO}_4)_2$. The upper curve illustrates the observed data, while the lower curve is the differences between observed and calculated data.

metal, phosphorous, and oxygen atoms). The occupancy parameters were refined with constraints according to stoichiometry. The angular dependence of the peak FWHM (full-width in 2θ at half-maximum) was described by the usual quadratic form in $\tan(\theta)$

$$\text{FWHM}^2 = U \cdot \tan^2(\theta) + V \cdot \tan(\theta) + W.$$

Strong correlations were only found among the half width parameters and, for $(\text{Zn}_{0.40}\text{Mg}_{0.60})_3(\text{PO}_4)_2$, among the background coefficients.

Diagrams showing the observed powder intensity data for the four compositions are shown in Fig. 2. The Rietveld plot for $(\text{Zn}_{1-x}\text{Mg}_x)_3(\text{PO}_4)_2$ ($x = 0.27$) is shown in Fig. 3. Final R -values and other essential

data are summarized in Table II. The R_F value for the zinc-rich compound ($x = 0.27$) is remarkably low. All refinements have included an empirical correction for absorption (14). The final atomic parameters are given in Table III.

Discussion

The structure is built of distorted $(M1)\text{O}_5$ polyhedra and rather regular $(M2)\text{O}_6$ octahedra and PO_4 tetrahedra (see Fig. 1). Some interatomic distances and angles are given in Table IV. The standard deviations as obtained from the computer program (12) may be multiplied by correction factors to give "probable errors" with regard to serial correlations by the procedure described by Bé-

TABLE II
ESSENTIAL DATA FROM THE FINAL RIETVELD REFINEMENTS

	Zn ₇₃ Mg ₂₇	Zn ₅₀ Mg ₅₀	Zn ₄₀ Mg ₆₀	Zn ₂₀ Mg ₈₀
R_F	0.029	0.071	0.067	0.076
R_B	0.042	0.096	0.081	0.120
R_{wp}	0.059	0.076	0.035	0.061
d	0.43	0.31	0.93	0.36
N	274	274	274	274
$\text{FWHM}_{\min}(\text{°})$	0.112	0.114	0.107	0.115
$\text{FWHM}_{\max}(\text{°})$	0.202	0.194	0.150	0.250

Note. N = number of independent reflections; d = Durbin-Watson statistic d -value according to Hill and Flack (13); R_F = structure factor R -value. Other parameters defined as in Ref. (12). Zn₇₃Mg₂₇ stands for (Zn_{0.73}Mg_{0.27})₃(PO₄)₂, and so on.

TABLE III
ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS (Å²)

Atom	Zn ₇₃ Mg ₂₇	Zn ₅₀ Mg ₅₀	Zn ₄₀ Mg ₆₀	Zn ₂₀ Mg ₈₀
M1 occupancy	Zn _{0.918} Mg _{0.082}	Zn _{0.697} Mg _{0.303}	Zn _{0.567} Mg _{0.433}	Zn _{0.291} Mg _{0.709}
x	0.6176(1)	0.6155(2)	0.6136(2)	0.6121(5)
y	0.1392(1)	0.1389(2)	0.1396(2)	0.1391(4)
z	0.0842(2)	0.0859(4)	0.0900(3)	0.0926(7)
M2 occupancy	Zn _{0.354} Mg _{0.646}	Zn _{0.106} Mg _{0.894}	Zn _{0.066} Mg _{0.934}	Zn _{0.018} Mg _{0.982}
B(M1,M2)^a	2.30(4)	2.06(7)	1.66(6)	2.80(9)
P x	0.1989(3)	0.1992(4)	0.1996(4)	0.1991(6)
y	0.1927(3)	0.1948(4)	0.1945(3)	0.1966(5)
z	0.0366(4)	0.0369(6)	0.0349(5)	0.0354(9)
B(P)	2.45(6)	2.69(9)	1.70(8)	3.08(10)
O1 x	0.0534(6)	0.0595(8)	0.0587(7)	0.0621(10)
y	0.1338(6)	0.1384(8)	0.1399(7)	0.1430(10)
z	0.8236(8)	0.8217(11)	0.8205(10)	0.8229(14)
O2 x	0.1289(7)	0.1309(10)	0.1276(8)	0.1247(12)
y	0.1946(6)	0.1943(8)	0.1951(7)	0.1952(10)
z	0.3094(10)	0.3031(14)	0.3069(11)	0.3080(16)
O3 x	0.2577(5)	0.2615(7)	0.2595(6)	0.2633(10)
y	0.3575(6)	0.3617(8)	0.3616(7)	0.3633(10)
z	0.9427(8)	0.9435(12)	0.9403(10)	0.9398(15)
O4 x	0.3605(6)	0.3584(9)	0.3605(7)	0.3593(11)
y	0.0778(5)	0.0751(7)	0.0770(6)	0.0787(9)
z	0.0556(9)	0.0491(12)	0.0518(10)	0.0426(16)
B(oxygen)	2.17(7)	2.15(10)	1.71(9)	2.46(13)

Note. Zn₇₃Mg₂₇ stands for (Zn_{0.73}Mg_{0.27})₃(PO₄)₂, and so on. * Space group $P2_1/n$ (No. 14) with the equivalent positions $\pm(x, y, z)$, $\pm(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$.

^a Atom M2 fixed at (0, 0, $\frac{1}{2}$).

TABLE IV
SOME INTERATOMIC DISTANCES (Å) AND ANGLES (°)

	$\text{Zn}_{73}\text{Mg}_{27}$	$\text{Zn}_{50}\text{Mg}_{50}$	$\text{Zn}_{40}\text{Mg}_{60}$	$\text{Zn}_{20}\text{Mg}_{80}$	Mg_{100}^a
M1-O1	2.32(1)	2.26(2)	2.23(1)	2.19(2)	2.142(7)
M1-O2	1.97(1)	2.00(2)	1.99(1)	2.00(2)	1.965(8)
M1-O3	2.02(1)	2.04(2)	2.02(1)	2.03(2)	2.063(8)
M1-O4	2.00(1)	2.01(2)	1.98(1)	1.98(2)	2.012(5)
M1-O4'	1.96(1)	1.92(2)	1.95(1)	1.94(2)	1.961(6)
Mean	2.05	2.05	2.03	2.03	2.028
M2-O1 (×2)	1.99(1)	2.01(2)	2.02(1)	2.04(2)	2.034(8)
M2-O2 (×2)	2.16(1)	2.18(2)	2.16(1)	2.14(2)	2.179(6)
M2-O3 (×2)	2.18(1)	2.14(2)	2.16(1)	2.12(2)	2.150(5)
Mean	2.11	2.11	2.11	2.10	2.121
P-O1	1.55(1)	1.53(2)	1.53(1)	1.51(2)	1.535(8)
P-O2	1.52(1)	1.48(2)	1.52(1)	1.53(2)	1.508(8)
P-O3	1.54(1)	1.55(2)	1.55(1)	1.55(2)	1.534(6)
P-O4	1.55(1)	1.56(2)	1.56(1)	1.56(2)	1.527(5)
Mean	1.54	1.53	1.54	1.54	1.526
O1-P-O2	110.6(6)	111.9(12)	111.3(6)	111.2(14)	111.77
O1-P-O3	106.1(6)	105.5(12)	104.5(6)	104.7(14)	103.72
O1-P-O4	110.7(6)	108.6(12)	110.7(6)	109.2(14)	110.43
O2-P-O3	113.8(6)	114.7(12)	114.4(6)	115.8(14)	112.08
O2-P-O4	106.6(6)	106.8(12)	106.7(6)	108.3(14)	108.61
O3-P-O4	109.1(6)	109.2(12)	109.2(6)	107.4(14)	110.19
Mean	109.5	109.4	109.5	109.4	109.46
O1-M1-O2 ^b	79.4(5)	80.5(8)	80.6(4)	81.0(9)	83.52
O1-M1-O3	68.8(4)	69.2(7)	69.8(4)	69.8(9)	70.02
O1-M1-O4	90.1(4)	92.4(7)	92.6(4)	94.0(9)	94.53
O4-M1-O4'	81.3(5)	81.4(9)	81.3(5)	81.7(9)	82.12
O1-M2-O2 ^c	82.9(5)	82.3(8)	81.7(4)	81.2(9)	81.03
O1-M2-O3	95.2(4)	94.0(7)	93.6(4)	92.8(9)	94.03
O2-M2-O3	93.7(5)	92.8(8)	93.3(8)	93.8(9)	93.16

Note. $\text{Zn}_{73}\text{Mg}_{27}$ stands for $(\text{Zn}_{0.73}\text{Mg}_{0.27})_3(\text{PO}_4)_2$, and so on. "Probable errors" as defined by Bérar and Lelann (15) are in parentheses.

^a Data for $\gamma\text{-Mg}_3(\text{PO}_4)_2$ from Ref. (10).

^b For the five-coordinated M1 site only angles $< 100^\circ$ are given.

^c From the space group symmetry, the following general relations hold for the six-coordinated M2 site:

$$\text{OX-M2-OY} (= \text{OX}'\text{-M2-OY}') = \phi \quad (X \text{ and } Y = 1, 2, \text{ or } 3)$$

then

$$\begin{aligned} \text{OX-M2-OY}' (= \text{OX}'\text{-M2-OY}) &= 180 - \phi \\ \text{OX-M2-OX}' &= 180. \end{aligned}$$

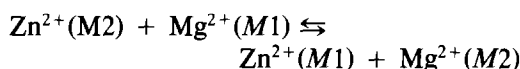
rar and Lelann (15). The factors for the four compositions are, in the order given in Table IV: 2.3, 2.9, 1.85, and 2.7.

Corresponding distances and angles in the four phases are consistent, thus reflecting

the good reproducibility of the refinement procedure. The average metal-oxygen distances are almost constant but with a slight decrease as the smaller Mg^{2+} ion replaces Zn^{2+} in the structure. The change in dis-

tance with composition is most noticeable for M1–O1, which decreases from 2.32 Å in the zinc-rich to 2.19 Å in the magnesium-rich phase. The P–O distances are reasonable, and the mean values in good agreement with the P–O grand mean of 1.537 Å as obtained for divalent-metal orthophosphates (1).

The cation distribution coefficient K_D for the exchange equilibrium



is conventionally defined as

$$K_D = \frac{[X_{\text{Zn}}(\text{M1}) \cdot X_{\text{Mg}}(\text{M2})]}{[X_{\text{Zn}}(\text{M2}) \cdot X_{\text{Mg}}(\text{M1})]}$$

Accordingly, the K_D coefficients here obtained for the solid solutions are 20, 19, 19, and 22. The last figure is very uncertain because of the small amount of zinc in the compound, however. On the basis of the present and the above cited earlier results (1, 3) we therefore conclude that the cation distribution coefficient K_D at 800°C for the $(\text{Zn}_{1-x}\text{Mg}_x)_3(\text{PO}_4)_2$ series is almost constant and around 20. Similar results of almost constant K_D values irrespective of composition have been demonstrated in the isostructural solid solution series $(\text{Zn}_{1-x}\text{Fe}_x)_3(\text{PO}_4)_2$ and $(\text{Mg}_{1-x}\text{Fe}_x)_3(\text{PO}_4)_2$ by means of ^{57}Fe Mössbauer spectroscopy (16). The NMR results published by Jakeman *et al.* (5) on phases quenched from 1000°C are therefore quite interesting. The discrepancy in the results may be due to difference in equilibrium temperature or on suggested (4) but hitherto not

demonstrated superstructures within this system.

Acknowledgments

This work has received financial support from the Swedish Natural Science Research Council and the Centre National de la Recherche Scientifique.

References

1. A. G. NORD, in "Stereochemistry of Organometallic and Inorganic Compounds" (I. Bernal, Ed.), Vol. I, pp. 50–145, Elsevier, Amsterdam and New York (1986).
2. A. G. NORD, *Mater. Res. Bull.* **12**, 563 (1977).
3. H. M. RIETVELD, *J. Appl. Crystallogr.* **2**, 65 (1969).
4. A. G. NORD AND T. STEFANIDIS, *Mater. Res. Bull.* **16**, 1121 (1981).
5. R. J. B. JAKEMAN, A. K. CHEETHAM, N. J. CLAYDEN, AND C. M. DOBSON, *J. Am. Chem. Soc.* **107**, 6249 (1985).
6. C. R. HUBBARD, H. E. SWANSON, AND F. A. MAUER, *J. Appl. Crystallogr.* **8**, 45 (1975).
7. P.-E. WERNER, *Ark. Kemi* **31**, 513 (1969).
8. P. M. DE WOLFF, *J. Appl. Crystallogr.* **1**, 108 (1968).
9. G. S. SMITH AND R. L. SNYDER, *J. Appl. Crystallogr.* **12**, 60 (1979).
10. A. G. NORD AND P. KIERKEGAARD, *Acta Chem. Scand.* **22**, 1466 (1968).
11. C. CALVO, *J. Phys. Chem. Solids* **24**, 141 (1963).
12. D. B. WILES, A. SAKTHIVEL, AND R. A. YOUNG, "User's Guide to Program DBW3.2S for Rietveld Analysis of X-ray and Neutron Powder Diffraction Patterns (Version 8804)," School of Physics, Georgia Institute of Technology, Atlanta.
13. R. J. HILL AND H. D. FLACK, *J. Appl. Crystallogr.* **20**, 356 (1987).
14. P.-E. WERNER AND M. WESTDAHL, to be published.
15. J. F. BÉRARD AND P. LELANN, *J. Appl. Crystallogr.* **24**, 1 (1991).
16. H. ANNERSTEN, T. ERICSSON, AND A. G. NORD, *J. Phys. Chem. Solids* **41**, 1235 (1980).