JOURNAL OF SOLID STATE CHEMISTRY 40, 131–135 (1981)

Crystal Chemistry of $M_{12}P_7$ Phases in Relation with the M_2P Phosphides

S. MAAREF AND R. MADAR
ENIG Gabès, Tunisia

AND P. CHAUDOUET, J. P. SENATEUR, AND R. FRUCHART
E.R. 155, IEG, Grenoble, France

Received November 3, 1980; in revised form June 17, 1981

A structural model for the description of transition metal phosphides has been applied to the determination of the structural relation between $M_{12}P_7$ and M_2P hexagonal phases. The correctness of this approach has been tested by the prediction of the substitutional ordering in $M_{12}P_7$ phases.

Introduction

The phosphides of transition metal with M_2P composition (M = Ni, Co, Fe, Mn, . . .) have been usefully described in terms of polyhedra formed by phosphorus atoms (*1*, *2*). Based on this description, the crystal chemistry of these phases has been widely studied during the last 10 years (*3*). Occasionally, as in the case of oxides, the substitutional order can be correlated with the nonmetal surrounding of the transition metal site (*4*, *5*). The influence of the four major factors (size, number of *d* electrons, electronegativity, crystal field effects) has been evaluated. We sought to investigate if the same principles can be applied to other transition metal phosphides with a composition slightly different from 2: 1. The closest ones reported up to now have the formula $M_{1.7}P$ as for instance $Cr_{12}P_7$. Several workers have already reported structural data for this chromium phosphide but certain features remain ambiguous (*6*, *7*). The availability of single crystals of this phase has permitted the redetermination of the crystal structure (*8*) and the establishment of structural relations between this structure and that of Fe_2P. The determined structural model was checked by X-ray diffraction and Mössbauer spectroscopy on substituted phases.

Experimental

Shiny dark brown crystals of $Cr_{12}P_7$ were grown by chemical vapor transport. Elemental components, chromium powder and red phosphorus were placed into 11-mm-id, 18-cm-long silica tubes and evacuated to less than 1 Torr. Chlorine gas was then introduced to produce a partial pressure of 100 Torr at room temperature. The tubes were sealed and transport was attempted at several charge and growth zone temperatures. The best conditions for successful

0022-4596/81/140131-05$02.00/0

transport are as follows:

Temperature of the hot zone : 1300 K
Temperature of the cold zone : 1240 K
Charge composition : $Cr_{1.5}P_{1.0}$

The crystals grow in the form of needles of millimeter size in the hot part of the quartz tube. Some of these crystals were ground into powder and analyzed by X-ray diffraction using silicon as an internal standard. These crystals were found single phase $Cr_{12}P_7$ with lattice constants of the hexagonal cell:

$$a = 8.966 \text{ Å}, \quad c = 3.311 \text{ Å};$$

the composition of the single crystals was checked by density measurements, thermogravimetry, and chemical analysis.

The substituted phases $Cr_{12-x}M_xP_7$ (M = Mn, Fe) were synthetized in powdered form by solid-state diffusion in quartz ampoules under vacuum at 1200 K; these compounds were analysed by X-ray diffraction and Mössbauer spectroscopy. The measurements were made at room temperature using a parabolic motion Mössbauer spectrometer coupled to a multichannel analyzer operating in the time mode. The source was ^{57}Co diffused in palladium and the system was calibrated by the Mössbauer spectrum of a high-purity iron sample. The positions, widths and amplitudes of the peaks were fitted by a least-squares program (*9*).

Results and Discussion

The structure has been determined by Chun and Carpenter (*8*) at Brown University.

The crystals of $Cr_{12}P_7$ were found to be hexagonal, space group $P6_3/m$, isostructural with Th_7S_{12}. One phosphorus atom is disordered between two positions and half of the chromium atoms exhibit disorder coupled to that of the phosphorus atoms. Also additional weak reflections, as observed by Chun and Carpenter (*8*) in Weissenberg and precession photographs of the layer 1 = 0 revealed the existence of a superlattice with a cell seven times that of the original one. Despite many attempts, no model consistent with the data has been found. Our approach to this problem was at first to try to understand the crystal chemistry of this phase in relation with previous work done in M_2P compounds.

In this way the structure of $Cr_{12}P_7$ can be usefully described in term of polyhedra formed by phosphorus atoms like in the case of M_2P phosphides. Chromium atoms are coordinated by either five phosphorus atoms in a distorted square pyramid or by four in a distorted tetrahedral arrangement. Phosphorus atoms divide the crystal into polyhedra of three kinds:

—square pyramids,
—tetrahedra,
—trigonal prisms.

Pyramids and tetrahedra alternate along columns, prisms are stacked one above another to form another kind of columns. Both types of columns are parallel to the *c* axis and both project into triangles as shown in Fig. 1. In the M_2P-type structure we have only observed the kind of columns formed by the superposition of square pyramids and tetrahedra. Based on this description we may consider 26 polyhedra in a $Cr_{12}P_7$ unit cell: 18 pyramids, 6 tetrahedra,

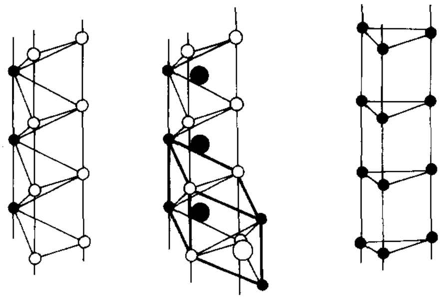

FIG. 1. Different kinds of sites in the $Cr_{12}P_7$ structure.

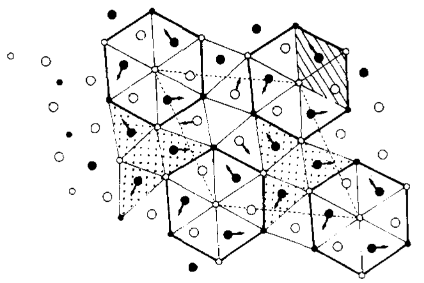

FIG. 2. Schematic representation of the $Cr_{12}P_7$ structure. Arrows are parallel to the axis of the pyramids. Black circles : $z = \frac{1}{2}$; white circles : $z = 0$. Big circles : Cr; little circles : P.

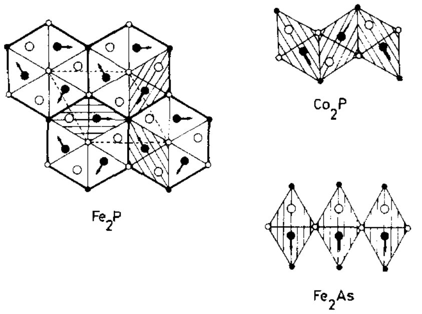

FIG. 3. Schematic representation of the M_2X structures. Arrows are parallel to the axis of the pyramids. Black circles : $z = \frac{1}{2}$; white circles : $z = 0$. Big circles : Cr; little circles : X atoms.

and 2 prisms. Half of the pyramids and tetrahedra are occupied by the 12 chromium atoms whereas all prisms are empty (Fig. 2). In the case of M_2P hexagonal structure there is an equal number of pyramidal and tetrahedral sites, half of them being occupied (Fig. 3). By analogy the $Cr_{12}P_7$ compound may be usefully written as $Cr_9^PCr_3^T\square_2^{PR}P_7$ where Cr^P, Cr^T, and $\square^{PR}$ represent respectively a chromium atom in a pyramidal site, a tetrahedral site, and an empty prismatic site. In principle the substitution of a chromium atom by another transition metal atom may occur in the two occupied sites, as observed in the M_2P type compounds. In the case of M_2P type compounds, two extreme situations can be found:

—the substitution of chromium by iron in Cr_2P is total an ordered: for the composition CrFeP the iron atoms are located only in the tetrahedral site as determined by neutron diffraction and Mössbauer spectroscopy

—the substitution of chromium by manganese is also total but almost entirely disordered as determined by neutron diffraction.

To check if the ordering mechanism is still valid for the $M_{12}P_7$ phase we have prepared solid solutions $Cr_{12-x}Fe_xP_7$ and $Cr_{12-x}Mn_xP_7$. The compounds were single phase for $0 < x < 3$ in the first case and for $0 < x < 6$ in the second case.

The variations of the hexagonal cell parameters are linear as a function of substitution for both systems. However, the variation is much more pronounced for iron substitution than for manganese substitution (Fig. 4). The same kind of effect has been already reported in the case of MM'P compounds, where it has been related to the substitutional order. This was the first indication of an ordered substitution in the case of $Cr_{12-x}Fe_xP_7$. The final analysis of the substitutional order was made by Mössbauer spectroscopy on the $Cr_9Fe_3P_7$ composition, limit of the solid solution. The Mössbauer spectrum (Fig. 5) is the superposition of two symmetrical doublets with the following parameters at 295 K.

Site 1: Intensity 0.85, $\delta = 0.218 \pm 0.002$ mm/sec, $e^2qQ/2 = 0.474 \pm 0.002$ mm/sec;
Site 2: Intensity 0.15, $\delta = 0.44 \pm 0.01$ mm/sec, $e^2qQ/2 = 0.62 \pm 0.01$ mm/sec.

The isomer shifts for sites 1 and 2 have been found to be very similar to those obtained for the equivalent site (respectively T and P site) in the M_2P structures

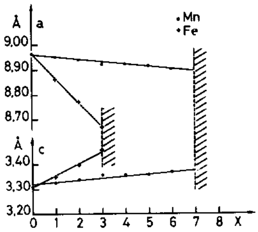

FIG. 4. Hexagonal unit cell parameters in the solid solution $Cr_{12-x}M_xP_7$.

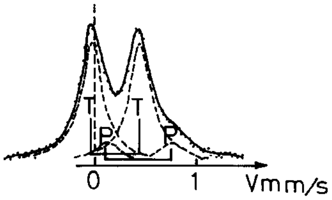

FIG. 5. Mössbauer spectrum of $Cr_9Fe_3P_7$.

(Table I). Assuming equal Mössbauer factors on the two sites, the peak intensity ratio gives directly the iron occupancy ratio in the compound. As it seems very doubtful that iron can enter the empty prismatic sites, the main result is that even with nine pyramidal sites available for only three tetrahedral ones in the $Cr_{12}P_7$ structure, the substitution of chromium by iron has occurred almost entirely in the tetrahedral site, where 85% of iron atoms are located.

Conclusion

The model previously used for the description of transition metal phosphides M_2P has been applied to the description of the $Cr_{12}P_7$-type structure. A strong structural relation has been established between the two structures, especially the presence of the same hexagonal building blocks formed by the junction of three tetrahedral and three pyramidal sites. Based on this description the substitutional ordering can be predicted in the $Cr_{12}P_7$ structure on the same basis as that previously used for the M_2P structure. This relation was checked in the case of the ordered solid solutions $Cr_{12-x}Fe_xP_7$, where the substitution of chromium by iron has almost entirely occurred on the tetrahedral site. In the same way, the substitution of chromium by manganese must be disordered. This is in agreement with the existence of a large range of substitution and with the variation of the unit cell parameters versus the manganese content, but must be definitively determined by neutron diffraction. The same substitutional ordering has been already observed in the Cr_2P phase for the manganese and iron atoms (*4*).

The main difference between the two structures is due to the existence of empty prismatic sites in the $Cr_{12}P_7$ structure. However as recently reported (*10*, *11*) this prismatic site may be occupied either by a

TABLE I

MÖSSBAUER CHARACTERISTICS OF $M_{1-x}Fe_{1+x}P$ COMPOUNDS

	Iron in tetrahedral site			Iron in pyramidal site			
	S (mm/sec)	$e^2qQ/2$ (mm/sec)	I	S (mm/sec)	$e^2qQ/2$ (mm/sec)	I	T (K)
$Cr_{0.8}Fe_{1.2}P$	0.175 ± 0.008	0.25 ± 0.008	0.75	0.54 ± 0.01	0.68 ± 0.01	0.25	295
$Mn_{0.7}Fe_{1.3}P$	0.238 ± 0.006	0.14 ± 0.006	0.67	0.57 ± 0.006	0.65 ± 0.006	0.33	295
CoFeP	0.12 ± 0.01	≃0.1	0.14	0.52 ± 0.01	0.77 ± 0.01	0.86	450
NiFeP	0.32 ± 0.01	0.16 ± 0.01	0.25	0.576 ± 0.005	0.86 ± 0.005	0.75	295

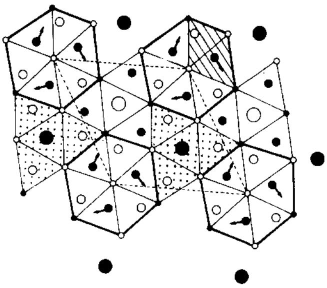

FIG. 6. Schematic representation of the $Ln_2M_{12}P_7$ structure. Arrows are parallel to the axis of the pyramids. Black circles: $z = \frac{1}{2}$; white circles: $z = 0$. Big circles: Ln atoms; medium circles: M atoms; small circles: P atoms.

rare earth or by a phosphorus atom, leading to the formula $Ln_2M_{12}P_7$ and $M_6M'_6P_9$, respectively. The main effect of this occupation is the inversion of the number of tetrahedral and pyramidal sites; for example, $Ln_2M_{12}P_7$ may be written (Fig. 6)

$$Ln_2^{PR}M_9^{T}M_3^{P}P_7.$$

The crystal chemistry and related physical properties of these phases will be reported soon.

References

1. A. ROGER, J. P. SENATEUR, AND R. FRUCHART, *Ann. Chim* **4**, 79 (1969).
2. R. FRUCHART, A. ROGER, AND J. P. SENATEUR, *J. Appl. Phys.* **40**, 3 (1969).
3. MME ROY MONTREUIL, AND B. DEYRIS, *Mater. Res. Bull.* **7**, 813 (1972).
4. J. P. SENATEUR, AND D. FRUCHART, *J. Phys. Colloq. C7* **12**, 38 (1977).
5. A. NYLUND, A. ROGER, J. P. SENATEUR, AND R. FRUCHART, *J. Solid State Chem.* **4**, 115 (1972).
6. B. ARONSSON, T. LUNDSTRÖM, AND S. RUNDQVIST, "Borides, Silicides and Phosphides" p. 26. Methuen London (1965).
7. H. E. BAURECHT, H. BOLLER, AND H. NOWOTNY, *Monatsh Chem.* **102**, 373 (1971).
8. H. K. CHUN, AND G. B. CARPENTER, *Acta Crystallogr. Sect. B* **35**, 30 (1979).
9. G. LECAER, Thèse Nancy I (1974).
10. W. JEITSCHKO, D. J. BRAUN, R. H. ASHCRAFT, AND R. MARCHAND, *J. Solid State Chem.* **25**, 309 (1978).
11. R. GUERIN, M. POTEL, AND M. SERGENT, "Abstracts 6th International Conference on Solid Compounds of Transition Elements, Stuttgart, June 1979.