frequently observed in condensed phosphate chemistry.

Main interatomic distances in these various polyhedra are given in Tables 3 and 4 which also report the main geometrical features of the two three-dimensional hydrogen-bond schemes.

Fig. 1 is a projection along the *c* axis of the sodium ammonium salt and Fig. 2 a projection along the *a* axis of the sodium rubidium compound. In both figures, the hydrogen atoms have been omitted. The drawings were prepared using the *STRUPLO* program (Fischer, 1985).

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Structure of Mixed-Valent Titanium Silicophosphates, $KTi_3P_6Si_2O_{25}$ and $CsTi_3P_6Si_2O_{25}$

BY A. BENMOUSSA, M. M. BOREL, A. GRANDIN, A. LECLAIRE* AND B. RAVEAU

Laboratoire de Cristallographie et Sciences des Matériaux, CRISMAT, ISMRa, Boulevard du Maréchal Juin, 14050 *Caen CEDEX, France*

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Abstract. $KTi_3P_6Si_2O_{25}$, $M_r = 824{\cdot}80$, trigonal, $P\bar{3}1c$, $a = 8{\cdot}2648\,(9)$, $c = 17{\cdot}038\,(1)$ Å, $V = 1007{\cdot}9\,(3)$ Å^3, $Z = 2$, $D_x = 2{\cdot}72$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 2{\cdot}07$ mm^{-1}, $F(000) = 403$, $T = 294$ K, $R = 0{\cdot}036$, $wR = 0{\cdot}043$ for 1438 reflections with $I > 3\sigma(I)$ out of 4577 unique reflections measured. $CsTi_3P_6Si_2O_{25}$, $M_r = 918{\cdot}60$, trigonal, $P\bar{3}1c$, $a = 8{\cdot}2145\,(6)$, $c = 17{\cdot}249\,(1)$ Å, $V = 1008{\cdot}0\,(2)$ Å^3, $Z = 2$, $D_x = 3{\cdot}03$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 3{\cdot}63$ mm^{-1}, $F(000) = 439$, $T = 294$ K, $R = 0{\cdot}034$, $wR = 0{\cdot}039$ for 1655 reflections with $I > 3\sigma(I)$ out of 4547 unique reflections measured. The '$Ti_3P_6Si_2O_{25}$' host lattice is built up from corner-sharing TiO_6 octahedra and PO_4 and SiO_4 tetrahedra, which form wide tunnels in which the K or Cs ions are located. In the titanium and molybdenum silicophosphates, the thermal motion of the *A* ion in the tunnel increases rapidly as the difference between the *A*—O length and the sum of the ionic radii increases.

Introduction. During the investigation of the system *A*–Mo–P–Si–O, the silicomolybdenophosphates $AMo_3P_6Si_2O_{25}$ (A = K, Rb, Tl, Cs) (Leclaire, Borel, Grandin & Raveau, 1985; Leclaire, Monier & Raveau, 1984, 1985), MoP_3SiO_{11} (Leclaire & Raveau, 1987), $Mo_4P_6Si_2O_{25}$ (Leclaire, Lamire & Raveau, 1988) and $Mo_2P_4Si_4O_{23}$ (Leclaire, Borel, Grandin & Raveau, 1989) were isolated. The oxides $AMo_3P_6Si_2O_{25}$ exhibit a particular behaviour with respect to the valency of molybdenum. This latter element is characterized here by mixed valency (Mo^{III}–Mo^{IV}) which cannot lead to electronic delocalization since the MoO_6 octahedra are isolated, *i.e.* are linked to each other through PO_4 tetrahedra. From the crystal structure, it appears that two sites are available for molybdenum, Mo(1) located within the layers and Mo(2) bridging the layers. The number of sites suggests that they are occupied in an ordered way by Mo^{IV} and Mo^{III} respectively, according to the formula $AMo_2^{IV}Mo^{III}P_6Si_2O_{25}$. However, an examination of the Mo—O bond lengths shows clearly that this type of ordering of Mo^{IV} and Mo^{III} does not exist. Thus, although the Mo(1)—O distances are longer than the Mo(2)—O distances, indicating that the valency of Mo(2) is greater than that of Mo(1), the mean length of the Mo(1)—O bonds is intermediate between that of the Mo(2)—O bonds and the mean values of the Mo^{III}—O bonds observed for MoP_3SiO_{11} and $Mo_4P_6Si_2O_{25}$. This leads to the conclusion that molybdenum exhibits a mixed valency, Mo^{III}–Mo^{IV}, within the $Mo_2P_6Si_2O_{25}$ layers whereas it is tetravalent between these layers. In order to determine whether this phenomenon could be generalized to the other $AM_3P_6Si_2O_{25}$ members of the series, the crystal growth of silicophosphates of titanium was undertaken. We report here

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* To whom correspondence should be addressed.

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Table 1. *Atomic coordinates and equivalent isotropic thermal parameters and their e.s.d.'s*

Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta) \times B(1,3) + bc(\cos\alpha)B(2,3)]$.

	x	y	z	B_{eq}(Å^2)
$KTi_3P_6Si_2O_{25}$ (1)				
K	0·333	−0·333	0·250	6·81 (8)
Ti(1)	0·333	−0·333	0·02516 (4)	0·417 (6)
Ti(2)	−0·333	0·333	0·250	0·499 (9)
P	0·38255 (8)	0·3315 (1)	0·11022 (4)	0·517 (8)
Si	0·000	0·000	0·09281 (9)	0·80 (1)
O(1)	0·1190 (3)	−0·4009 (3)	0·0953 (2)	1·27 (4)
O(2)	−0·1868 (3)	0·2566 (3)	0·4576 (1)	1·12 (4)
O(3)	0·4784 (3)	0·3386 (4)	0·1865 (1)	1·93 (5)
O(4)	0·000	0·000	0·000	1·54 (7)
O(5)	0·0235 (3)	−0·1690 (3)	0·1264 (1)	1·20 (4)
$CsTi_3P_6Si_2O_{25}$ (2)				
Cs	0·333	−0·333	0·250	2·335 (7)
Ti(1)	0·333	−0·333	0·02293 (4)	0·372 (6)
Ti(2)	−0·333	0·333	0·250	0·368 (8)
P	0·38368 (8)	0·3311 (1)	0·10965 (4)	0·399 (8)
Si	0·000	0·000	0·09176 (8)	0·62 (1)
O(1)	0·1147 (3)	−0·4074 (3)	0·0906 (1)	0·93 (3)
O(2)	−0·1944 (3)	0·2473 (3)	0·4552 (1)	0·85 (3)
O(3)	0·4789 (3)	0·3420 (4)	0·1861 (1)	1·33 (4)
O(4)	0·000	0·000	0·000	1·24 (6)
O(5)	0·0278 (3)	−0·1678 (3)	0·1259 (1)	0·96 (3)

Table 2. *Main atomic bonds* (Å)

	$KTi_3P_6Si_2O_{25}$ (1)	$CsTi_3P_6Si_2O_{25}$ (2)
Ti(1)—O(1) × 3	1·972 (2)	1·966 (2)
Ti(1)—O(2) × 3	1·991 (2)	1·993 (2)
Ti(2)—O(3) × 6	1·914 (2)	1·926 (2)
P—O(1^i)	1·508 (2)	1·527 (2)
P—O(2^{ii})	1·511 (2)	1·511 (2)
P—O(3)	1·508 (2)	1·513 (2)
P—O(5^i)	1·576 (2)	1·577 (2)
Si—O(4)	1·581 (1)	1·583 (1)
Si—O(5) × 3	1·608 (2)	1·617 (2)
A—O(1) × 6	3·068 (2)	3·172 (2)

Symmetry code: (i) $-y, x-y, z$; (ii) $y-x, y, 0{\cdot}5-z$.

on the single-crystal structure determination of the potassium and caesium silicophosphates of titanium, $KTi_3P_6Si_2O_{25}$ (1) and $CsTi_3P_6Si_2O_{25}$ (2).

Experimental. Crystal dimensions: 0·144 × 0·12 × 0·096 (1), 0·120 × 0·09 × 0·072 mm (2). Enraf–Nonius diffractometer. Unit-cell dimensions determined by least squares on 25 reflections $\pm 2\theta$, $18 \le \theta \le 22°$. Intensity measurements up to $\theta = 45°$ with an ω–$4/3\theta$ scan of $(1 + 0{\cdot}35\tan\theta)°$ width and a counter slit aperture of $(1 + \tan\theta)$ mm; values determined by a study of reflections in the ω–θ plane [h − 14→8, k 0→16, l 0→32 (1); h − 13→8, k 0→16, l 0→34 (2)]. Scanning speed adjusted to obtain $\sigma(I)/I < 0{\cdot}018$ or to approach it in 60 s. Three standards (440, 0,3,14, 3,3,14) monitored for counting every 2000 s and for orientation every 600 reflections: no appreciable trends. No corrections made for extinction or absorption. Heavy-atom method. Full-matrix least-squares refinement on F. Usual f' and f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV). 58 parameters refined, $R = 0{\cdot}036$, $wR = 0{\cdot}043$, $S = 1{\cdot}30$, for (1); 58 parameters refined, $R = 0{\cdot}034$, $wR = 0{\cdot}039$, $S = 1{\cdot}33$, for (2). $\Delta/\sigma < 0{\cdot}005$, $\Delta\rho < 1$ e Å^{-3}, $w = 1/\sigma^2(F)$. Calculations performed on a MicroVAX II computer with the *SDP* System (B. A. Frenz & Associates, Inc., 1982). Atomic parameters are given in Table 1.*

Discussion. The host lattice (Fig. 1), built up from corner-sharing TiO_6 octahedra and PO_4 and SiO_4 tetrahedra, is quite similar to those observed for the $AMo_3P_6Si_2O_{25}$ compounds (Leclaire, Monier & Raveau 1984, 1985). The different polyhedra are

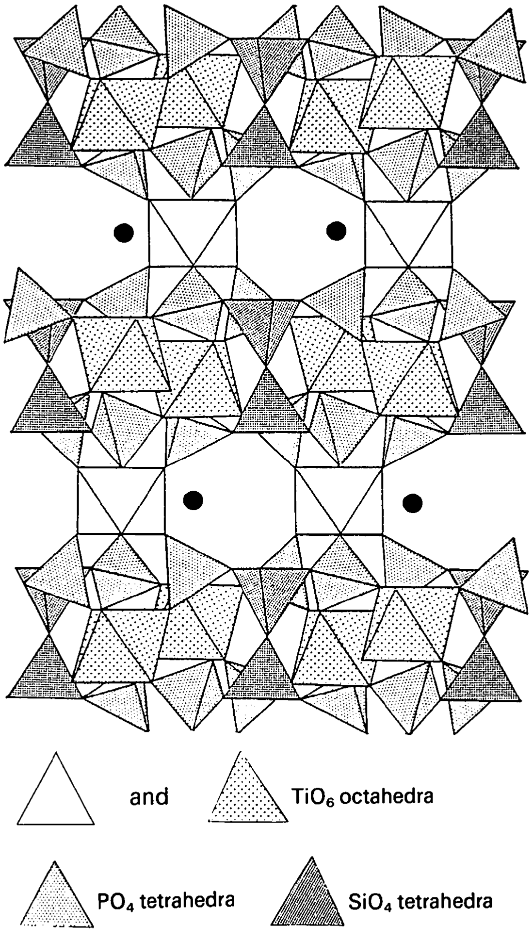

Fig. 1. Projection of the host-lattice structure along a showing the tunnels.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53680 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

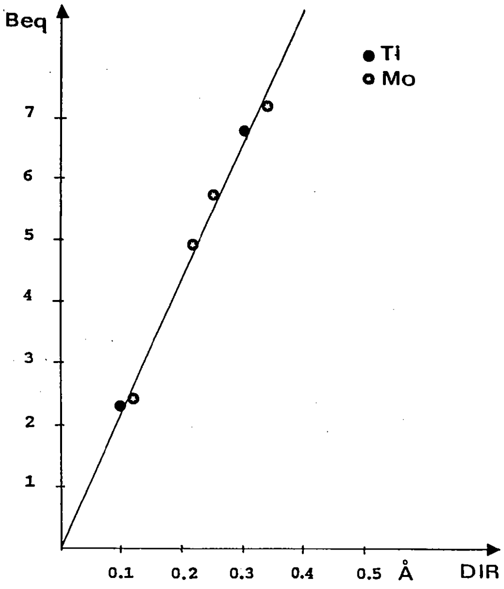

Fig. 2. Plot of B_{eq} (Å^2) *versus* DIR (Å).

almost regular and the interatomic distances in the K and Cs silicotitanophosphates are almost the same (Table 2).

The Ti(1)—O distances in the $Ti_2P_6Si_2O_{25}$ layers are longer than the Ti(2)—O bonds of the bridging octahedra, suggesting a Ti^{IV} valency for Ti(2) and a Ti^{IV}/Ti^{III} mixed valency within the layers. Thus, it is clear that the interlayer octahedra are preferentially occupied by smaller cations, Mo^{IV} or Ti^{IV} independently of their electronic structure.

The size of the tunnels is not greatly affected by the size of the A^+ ion. The A—O distances decrease from 3·172 to 3·068 Å when the sum of the ionic radii (Shannon, 1976) decreases from 3·07 to 2·77 Å; correspondingly, the thermal motion of the A ions increases significantly (2·34 to 6·81 Å^2) when the ionic radius decreases, as previously observed with the $AMo_3P_6Si_2O_{25}$ compounds.

A minor difference occurs between the Mo and the Ti compounds: the B_{eq} values of the A^+ ions are smaller in the Ti compounds owing to the smaller size of the tunnels. Thus, the parameter which determines the thermal motion of the A^+ ions is not the ionic radius but the difference between the A—O length and the sum of the ionic radii, $\mathrm{DIR} = D_{A—O} - (IR_O + IR_A)$. This relationship is demonstrated in Fig. 2, in which a marked linear increase of the B_{eq} values *versus* DIR can be seen.

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Structure du Sulfure de Fer et d'Antimoine, $FeSb_2S_4$ (Berthiérite)

PAR P. LEMOINE ET D. CARRÉ

Laboratoire de Chimie Minérale Structurale, associé au CNRS URA 200,
Faculté des Sciences Pharmaceutiques et Biologiques, 4 *Avenue de l'Observatoire*,
75270 *Paris CEDEX* 06, *France*

ET F. ROBERT

Laboratoire de Chimie des Métaux de Transition, associé au CNRS URA 419, *Université Pierre et Marie Curie*, 4 *Place Jussieu*, 75005 *Paris, France*

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Abstract. Diantimony iron tetrasulfide, $FeSb_2S_4$, $M_r = 427\cdot6$, orthorhombic, $Pnam$, $a = 11\cdot401$ (2), $b = 14\cdot148$ (3), $c = 3\cdot758$ (2) Å, $V = 606\cdot2$ (6) Å^3, $Z = 4$, D_m(293 K) = 4·5 (1), $D_x = 4\cdot68$ (3) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 12\cdot5$ mm^{-1}, $F(000) = 192$, $T = 293$ K, $R = 0\cdot018$ for 732 observed reflec-

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