BRIEF COMMUNICATION

$Pr_4V_5Si_4O_{22}$—A New Praseodymium Vanadium Oxosilicate with Chevkinite Structure

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$Pr_4V_5Si_4O_{22}$, a new praseodymium vanadium oxosilicate with chevkinite structure, has been prepared by heating $PrOCl/V_2O_5/NH_4Cl$ in an evacuated silica tube; the source of silicon is the reaction tube. It crystallizes in the monoclinic space group $C2/m$(No. 12) with cell dimensions $a = 13.410(2)$, $b = 5.5998(9)$, $c = 11.027(3)$ Å, $\beta = 100.57(2)°$, $V = 814.0(5)$ Å^3, and $Z = 2$, $D_{calc} = 5.23$ g/cm^3. The structure consists of PrO_8 bicapped trigonal prisms, VO_6 octahedra, and Si_2O_7 pyrosilicate groups. This compound has vanadium oxide layers which are similar to the rutile structure; the V–V distances across the shared octahedral edges are 2.7999 Å and vanadium ions are reduced to show average valence of +3.2. © 1995 Academic Press, Inc.

INTRODUCTION

$LnM(TiM)_2(TiO_4)_2(Si_2O_7)$ compounds ($Ln = La^{3+}$ – Sm^{3+}; $M = Fe^{2+}$, Co^{2+}, Ni^{2+}) with perrierite or chevkinite type structures (1, 2) have been prepared. All of them have two Ti–O octahedral chains which are parallel to the b-axis and form layers, but have different structural element bonds on both sides of the Ti–O octahedral layers (3, 4). $La_4Ti_9Si_4O_{30}$ [5], which consists of two layers of fused titanium(III/IV) oxide octahedral slabs showing a perrierite-related structure, has been prepared as the first oxocompound containing a first row early transition metal. In this paper, we prepared the oxocompound containing vanadium, $Pr_4V_5Si_4O_{22}$, which adopts a chevkinite structure.

EXPERIMENTAL

Preparation. A pressed pellet containing 77.0 mg PrOCl, 36.4 mg V_2O_5(AR), and about 40 mg NH_4Cl(AR) was sealed in an evacuated silica tube. PrOCl was prepared by dehydrating $PrCl_3 \cdot xH_2O$ at 700°C in air; $PrCl_3 \cdot$

xH_2O was obtained by dissolving Pr_6O_{11} (99.9%) in 12N HCl acid. The tube was heated at 200°C for 21 hr, and then at 300, 400, and 500°C for 24 hours each, and finally at 600°C for 1 hr; it was then cooled to room temperature. The tube was reheated to 500°C for 1 hr then heated to 900°C at the rate of 4.2°C/hr, held at 900°C for 1 hr, and cooled to room temperature. The silica tube was eroded and black needle-like crystal, which are stable in air, were found. EDAX analysis of a crystal showed that it contained Pr, V, and Si, but no Cl; the silicon came from the reaction tube.

X-Ray determination. A crystal with approximate dimensions $1.0 \times 0.1 \times 0.1$ mm was found to be suitable for single crystal X-Ray diffraction. The diffraction data were collectd on an Enraf-Nonius CAD4 diffractometer with graphite monochromator MoKα radiation ($\lambda = 0.71069$ Å). Unit cell dimensions of $a = 13.410(2)$ Å, $b = 5.5998(9)$ Å, $c = 11.027(3)$ Å, $\beta = 100.57(2)°$ were determined from least-squares refinement of 25 reflections within 2θ 7–14°. A total of 1962 independent reflections ($R_{int} = 7\%$) were collected within 2θ 2–70° for hkl: $h + k = 2n$. Lorentz-polarization, DECAY (less than 2%) and ψ corrections were applied. The unique 1296 reflections with $I > 3\sigma(I)$ were used in structure determination and refinement. The structure of the title compound was determined by the TEXSAN program using the centric space group $C2/m$; the Pr atoms were located by Patterson map and the other atoms by least-squares refinement and difference Fourier map. Final full matrix least-squares refinement for 71 variables converged to $R = 6.0\%$, $R_w = 7.0\%$, $S = 1.21$, $(\Delta/\sigma)_{max} = 0.01$, and second extinction coefficient $= 9.0 \times 10^{-7}$ with anisotropic thermal parameter correction of Pr, V, and Si atoms. The maximum and minimum peaks on the final difference Fourier map are 3.84 e/Å^3 and -2.97 e/Å^3, respectively. Final atomic positional and thermal parameters are given in Tables 1 and 2, and selected bond lengths and bond angles are given in Tables 3 and 4.

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TABLE 1
Positional Parameters and $B(eq)$ for $Pr_4V_5Si_4O_{22}$

Atom	Site	x	y	z	$B(eq)$
Pr(1)	4i	0.35698(7)	0	0.24271(8)	0.67(3)
Pr(2)	4i	0.07149(7)	0	0.24892(8)	0.87(3)
V(1)	2d	0	$\frac{1}{2}$	$\frac{1}{2}$	0.5(1)
V(2)	2c	0	0	$\frac{1}{2}$	0.4(1)
V(3)	4f	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	0.39(8)
V(4)	2b	0	$\frac{1}{2}$	0	0.3(1)
Si(1)	4i	0.7039(3)	0	0.2303(4)	0.2(1)
Si(2)	4i	0.8621(4)	0	0.0431(4)	0.5(1)
O(1)	4i	0.350(1)	0	0.487(1)	0.8(2)
O(2)	4i	0.1431(9)	0	0.478(1)	0.4(2)
O(3)	8j	0.4787(6)	−0.253(2)	0.3654(7)	0.6(1)
O(4)	8j	0.2256(6)	−0.262(2)	0.3136(7)	0.4(1)
O(5)	4i	0.592(1)	0	0.160(1)	1.3(2)
O(6)	4i	0.188(1)	0	0.099(1)	0.8(2)
O(7)	8j	0.4323(8)	−0.264(2)	0.086(1)	1.5(2)
O(8)	4i	0.786(1)	0	0.139(2)	2.3(3)

DISCUSSION

The crystal structure of the title compound is shown in Fig. 1. In the structure, Pr atoms coordinate to oxygen atoms with a bicapped trigonal prismatic geometry; the mean value of Pr–O bond lengths is 2.53 Å for Pr(1)–O and Pr(2)–O. V atoms adopt an octahedral geometry with oxygen atoms; the mean values of V–O bond lengths are 2.02 Å, 2.00 Å, 1.99 Å, and 2.03 Å for V(1)–O, V(2)–O, V(3)–O, and V(4)–O, respectively. Si atoms are tetrahedrally coordinated to oxygen atoms; the mean value of Si–O bond lengths is 1.60 Å for Si(1)–O and Si(2)–O and the mean values of O–Si–O bond angles are 109.4° for O–Si(1)–O and 109.2° for O–Si(2)–O. The Si(1)O$_4$ and Si(2)O$_4$ tetrahedra connect through corner-shared oxygen atoms, O(8), with a Si(1)–O(8)–Si(2) angle of 177° forming a pyrosilicate slab.

TABLE 2
U Values for $Pr_4V_5Si_4O_{22}$

Atom	$U11$	$U22$	$U33$	$U12$	$U13$	$U23$
Pr(1)	0.0062(4)	0.0154(5)	0.0038(4)	0	0.0011(3)	0
Pr(2)	0.0055(4)	0.0238(6)	0.0040(4)	0	0.0019(3)	0
V(1)	0.005(2)	0.009(2)	0.007(2)	0	0.003(1)	0
V(2)	0.008(2)	0.005(2)	0.004(1)	0	0.005(1)	0
V(3)	0.005(1)	0.006(1)	0.004(1)	−0.002(1)	0.0024(7)	0.0009(9)
V(4)	0.008(2)	0.004(2)	0.001(1)	0	−0.000(1)	0
Si(1)	0.005(2)	0.001(2)	0.002(2)	0	−0.002(1)	0
Si(2)	0.009(2)	0.007(2)	0.004(2)	0	0.004(1)	0

TABLE 3
Selected Bond Distances (Å) for $Pr_4V_5Si_4O_{22}$

Atom		Atom	Distance	Atom		Atom	Distance
Pr(1)	—	O(1)[a]	2.71(1)	Pr(2)	—	O(2)[a]	2.53(1)
	—	O(3)[a,b]	2.386(8)(2×)		—	O(3)[c,d]	2.387(8)(2×)
	—	O(4)[a,b]	2.523(8)(2×)		—	O(4)[a,b]	2.527(8)(2×)
	—	O(6)[a]	2.51(1)		—	O(6)[a]	2.47(1)
	—	O(7)[a,b]	2.61(1)(2×)		—	O(7)[c,d]	2.69(1)(2×)
V(1)	—	O(1)[d,e]	1.99(1)(2×)	V(2)	—	O(2)[a,h]	1.98(1)(2×)
	—	O(3)[d,e,f,g]	2.034(9)(4×)		—	O(3)[c,d,f,i]	2.011(9)(4×)
V(3)	—	O(1)[a,e]	1.960(9)(2×)	V(4)	—	O(5)[d,j]	1.96(1)(2×)
	—	O(2)[a,e]	1.987(8)(2×)		—	O(7)[d,g,j,k]	2.06(1)(4×)
	—	O(4)[b,f]	2.023(8)(2×)				
Si(1)	—	O(4)[l,m]	1.616(9)(2×)	Si(2)	—	O(6)[n]	1.59(1)(2×)
	—	O(5)[a]	1.56(1)		—	O(7)[l,m]	1.64(1)
	—	O(8)[a]	1.62(2)		—	O(8)[a]	1.60(2)
Pr(1)	—	Pr(2)[a]	3.842(2)				
Pr(1)	—	V(1)[o]	3.119(1)	Pr(2)	—	V(2)[a]	3.092(1)
V(1)	—	V(2)[a,p]	2.7999(5)(2×)	V(3)	—	V(3)[b,q]	2.7999(5)(2×)

Note. (a) (x, y, z); (b) $(x, -y, z)$; (c) $(x - \frac{1}{2}, -y - \frac{1}{2}, z)$; (d) $(x - \frac{1}{2}, \frac{1}{2} + y, z)$; (e) $(\frac{1}{2} - x, \frac{1}{2} - y, 1 - z)$; (f) $(\frac{1}{2} - x, \frac{1}{2} + y, 1 - z)$; (g) $(x - \frac{1}{2}, \frac{1}{2} + y, z)$; (h) $(-x, -y, 1 - z)$; (i) $(\frac{1}{2} - x, -y - \frac{1}{2}, 1 - z)$; (j) $(\frac{1}{2} - x, \frac{1}{2} - y, -z)$; (k) $(\frac{1}{2} - x, \frac{1}{2} + y, -z)$; (l) $(\frac{1}{2} + x, -y - \frac{1}{2}, z)$; (m) $(\frac{1}{2} + x, \frac{1}{2} + y, z)$; (n) $(1 - x, -y, -z)$; (o) $(\frac{1}{2} + x, y - \frac{1}{2}, z)$; (p) $(x, 1 + y, z)$; (q) $(x, 1 - y, z)$.

TABLE 4
Selected Bond Angles (°) for $Pr_4V_5Si_4O_{22}$

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
O(3)	Pr(1)	O(3)	72.9(4)	O(1)	V(1)	O(1)	180.00	V(3)	O(1)	V(3)	91.2(5)
O(3)	Pr(1)	O(6)	143.2(2)	O(1)	V(1)	O(3)	86.7(3)	V(3)	O(1)	V(1)	133.6(3)
O(3)	Pr(1)	O(4)	85.6(3)	O(1)	V(1)	O(3)	93.3(3)	V(3)	O(1)	Pr(1)	102.9(4)
O(3)	Pr(1)	O(4)	127.8(3)	O(3)	V(1)	O(3)	88.3(5)	V(1)	O(1)	Pr(1)	81.5(4)
O(3)	Pr(1)	O(7)	74.4(3)	O(3)	V(1)	O(3)	180(3)	V(2)	O(2)	V(3)	132.9(3)
O(3)	Pr(1)	O(7)	113.8(3)	O(3)	V(1)	O(3)	91.7(5)	V(2)	O(2)	Pr(2)	85.6(4)
O(3)	Pr(1)	O(1)	65.3(3)	O(2)	V(2)	O(2)	180.00	V(3)	O(2)	V(3)	89.6(5)
O(6)	Pr(1)	O(4)	66.1(3)	O(2)	V(2)	O(3)	85.4(3)	V(3)	O(2)	Pr(2)	104.7(4)
O(6)	Pr(1)	O(7)	89.8(3)	O(2)	V(2)	O(3)	94.6(3)	V(2)	O(3)	V(1)	87.6(3)
O(6)	Pr(1)	O(1)	115.7(4)	O(3)	V(2)	O(3)	86.9(5)	V(2)	O(3)	Pr(1)	144.8(4)
O(4)	Pr(1)	O(4)	71.0(4)	O(3)	V(2)	O(3)	180.00	V(2)	O(3)	Pr(2)	88.9(3)
O(4)	Pr(1)	O(7)	104.6(3)	O(3)	V(2)	O(3)	93.1(5)	V(1)	O(3)	Pr(1)	89.4(3)
O(4)	Pr(1)	O(7)	155.5(3)	O(1)	V(3)	O(1)	180.00	V(1)	O(3)	Pr(2)	141.2(4)
O(4)	Pr(1)	O(1)	62.5(3)	O(1)	V(3)	O(2)	88.6(3)	Pr(1)	O(3)	Pr(2)	114.2(3)
O(7)	Pr(1)	O(7)	69.0(5)	O(1)	V(3)	O(2)	91.4(3)	Si(1)	O(4)	V(3)	125.7(5)
O(7)	Pr(1)	O(1)	138.1(3)	O(1)	V(3)	O(4)	86.2(4)	Si(1)	O(4)	Pr(1)	111.5(4)
O(3)	Pr(2)	O(3)	70.9(4)	O(1)	V(3)	O(4)	93.8(4)	Si(1)	O(4)	Pr(2)	105.4(4)
O(3)	Pr(2)	O(6)	144.6(2)	O(2)	V(3)	O(2)	180(3)	V(3)	O(4)	Pr(1)	107.7(3)
O(3)	Pr(2)	O(4)	131.6(3)	O(2)	V(3)	O(4)	85.5(4)	V(3)	O(4)	Pr(2)	103.9(3)
O(3)	Pr(2)	O(4)	89.5(3)	O(2)	V(3)	O(4)	94.5(4)	Pr(1)	O(4)	Pr(2)	99.1(3)
O(3)	Pr(2)	O(2)	66.6(3)	O(4)	V(3)	O(4)	180(3)	Si(1)	O(5)	V(4)	147.0(9)
O(3)	Pr(2)	O(7)	72.9(3)	O(5)	V(4)	O(5)	180.00	Si(2)	O(6)	Pr(2)	117.0(7)
O(3)	Pr(2)	O(7)	106.1(3)	O(5)	V(4)	O(7)	80.9(4)	Si(2)	O(6)	Pr(1)	142.3(7)
O(6)	Pr(2)	O(4)	66.7(3)	O(5)	V(4)	O(7)	99.1(4)	Pr(2)	O(6)	Pr(1)	100.7(5)
O(6)	Pr(2)	O(2)	119.7(4)	O(7)	V(4)	O(7)	91.8(6)	Si(2)	O(7)	V(4)	136.1(6)
O(6)	Pr(2)	O(7)	90.1(3)	O(7)	V(4)	O(7)	88.2(6)	Si(2)	O(7)	Pr(1)	112.2(5)
O(4)	Pr(2)	O(4)	70.9(4)	O(7)	V(4)	O(7)	180(3)	Si(2)	O(7)	Pr(2)	95.1(5)
O(4)	Pr(2)	O(2)	65.0(3)	O(5)	Si(1)	O(4)	109.9(4)	V(4)	O(7)	Pr(1)	99.0(5)
O(4)	Pr(2)	O(7)	154.9(3)	O(5)	Si(1)	O(8)	113.0(8)	V(4)	O(7)	Pr(2)	110.5(4)
O(4)	Pr(2)	O(7)	109.6(3)	O(4)	Si(1)	O(4)	111.4(6)	Pr(1)	O(7)	Pr(2)	98.3(3)
O(2)	Pr(2)	O(7)	139.0(3)	O(4)	Si(1)	O(8)	106.3(5)	Si(2)	O(8)	Si(1)	177(1)
O(7)	Pr(2)	O(7)	59.0(5)	O(6)	Si(2)	O(8)	116.4(8)	O(7)	Si(2)	O(7)	107.3(8)
O(8)	Si(2)	O(7)	102.1(5)	O(6)	Si(2)	O(7)	113.8(5)				

Pr(1)O$_8$ and Pr(2)O$_8$ polyhedra are connected by sharing a face of O(6)–O(4)–O(4) with Pr(1)–Pr(2) distances of 3.841 Å. Each dimer of [Pr(1)Pr(2)O$_{13}$] shares four edges, O(3)–O(7), with another four dimers, creating a praseodymium oxide layer (see Fig. 2). V(1)O$_6$ and V(2)O$_6$ octahedra are edge-sharing through O(3)–O(3), forming an octahedral vanadium oxide chain along the b-axis; V(3)O$_6$ octahedra, through O(1)–O(2), form another octahedral vanadium oxide chain which is rotated 90° with respect to the first one. These two octahedral chains share O(1) and O(2) atoms to form a rutile-related vanadium oxide layer (see Fig. 3). V(4)O$_6$ octahedra and Si$_2$O pyrosilicate groups are located between two praseodymium oxide layers, creating a praseodymium vanadium silicate slab. The structure of the title compound is formed by stacking this praseodymium vanadium silicate slab and the vanadium oxide layer which show a quasi-2D chevkinite structure.

For the title compound, if we assigned Pr, Si, and O to oxidation states of +3, +4, and −2, respectively, then five V atoms (V(1), V(2), V(4) and two V(3)) will show a sum oxidation state of +16. From the valence contribution in the chevkinite structure compounds [1, 2], we assigned V(3) a +4 oxidation state and other V(V(1), V(2), V(4)) atoms a +3 oxidation state, bond valence calculations using the formula $s = \exp[-(R - R_0)/B]$ where $B = .37$, $R_0 = 1.743$ for V^{3+}–O and 1.784 for V^{4+}–O (6, 7) show that V(1), V(2), V(3), and V(4) are +2.85, +2.99, +3.45, +2.82 v.u., respectively; the sum valence of V(1), V(2), V(4), and two V(3) atoms is +15.55, which is almost equal to the assignment sum oxidation state of +16. In the reaction process, the vanadium ions are reduced from the valence of +5 to an average valence of +3.2. This may be due to the thermal decomposition of NH$_4$VO$_3$ from the reaction of V$_2$O$_5$ with NH$_4$Cl (8, 9) or to the oxidizing–reducing reaction of V$_2$O$_5$ with HCl (10,

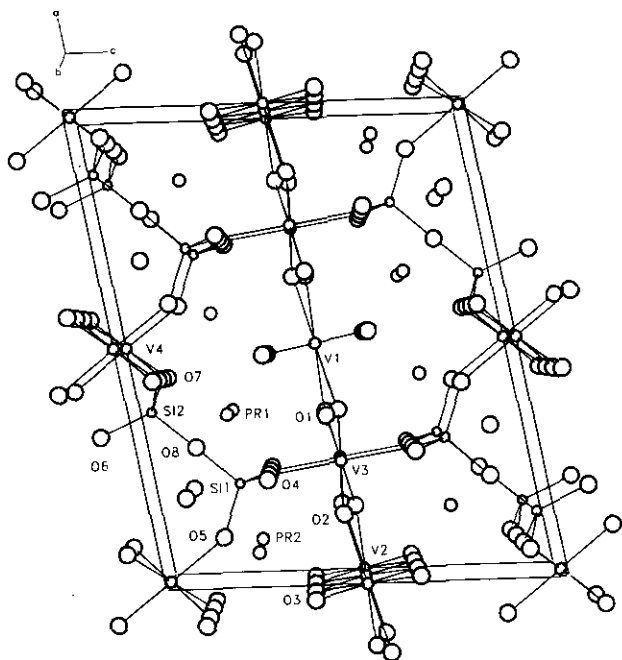FIG. 1. Crystal structure of $Pr_4V_5Si_4O_{22}$.

11) producing a lower oxidation state V processor species; then the processor species reacted with PrOCl and SiO_2 to produce the title compound with average vanadium oxidation state of +3.2. In here, some Cl_2 may be evolved in the reaction and NH_4Cl may serve as reaction agent as well as transport agent.

In the title compound, along the vanadium oxide chains, the V–V distances are 2.7999 Å, which is nearly 0.05 Å shorter than the V–V distances in rutile-like VO_2
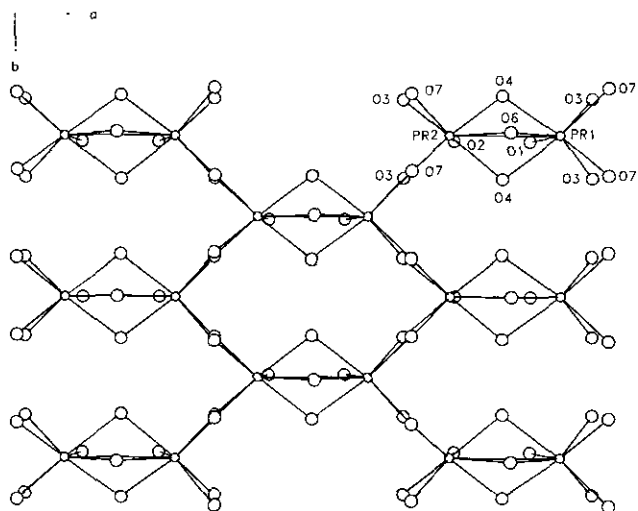
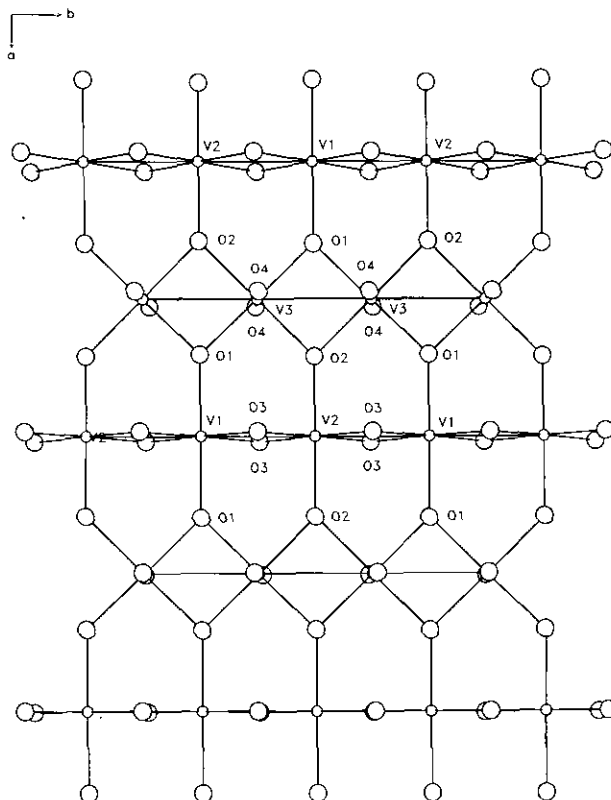FIG. 2. A view down [001] to show praseodymium oxide layer.

FIG. 3. A view down [001] to show vanadium oxide layer.

compound (12) and 0.08 Å shorter than that in corundum metallic V_2O_3 (13). From models created by Morin (14) and Goodenough (15, 16), these short V–V equidistances indicate the direct overlap of cationic d wave functions or strong covalent mixing of cationic $3d$ and anionic $2s$, $2p$ wave functions; thus we expect to see metallic conductivity.

ACKNOWLEDGMENTS

REFERENCES

1. J. Ito, Am. Miner. 52, 1094 (1967).
2. J. Ito and J. E. Arem, Am. Miner. 56, 307 (1971).
3. G. Gottardi, Am. Miner. 45, 1 (1960).
4. C. C. Peng and C. L. Pang, Sci. Sini. 13, 1539 (1964).
5. S. M. Wang and S.-J. Hwu, J. Am. Chem. Soc. 114, 6920 (1992).
6. I. D. Brown, Chem. Soc. Rev. 7, 359 (1978).
7. I. D. Brown and D. Altermatt, Acta Crystalogr. Sect. B 41, 244 (1985).
8. A. Deschanvres, G. Nouet, and B. Raveau, Compt. Rend. 261, 3144 (1965).

9. F. Theobald, R. Calara, and J. Bernald, *C. R. Acad. Sci. Ser. C* **266,** 1534 (1968).

10. R. J. H. Clark, *in* "Comprehensive Inorganic Chemistry" (J. C. Bailar, H. J. Emeleus, S. R. Nyholm, and A. F. Trotman-Dickenson, Eds.), Chap. 34. Pergamon, New York, 1973.

11. R. Beri, "Inorganic Chemistry," Tata McGraw–Hill, New Delhi, 1984.

12. K. V. Krishna Rao, S. V. Naidu, and L. Iyengar, *J. Phys. Soc. Jpn.* **23,** 1380 (1967).

13. P. D. Dernier, *J. Phys. Chem. Solids,* **31,** 2569 (1970).

14. F. J. Morin, *Phys. Rev. Lett.* **3,** 34 (1959).

15. J. B. Goodenough, "Magnetism and the Chemistry Bond." Interscience, New York, 1963.

16. J. B. Goodenough, *Phys. Rev.* **117,** 1442 (1960).