Crystal Structures and Lattice Distortions of σ-Type Layered Vanadium Bronzes: σ-$M_{0.25}$V$_2$O$_5$·H$_2$O (M = Mg, Co, Ni)

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New σ-type layered vanadium bronzes $M_{0.25}$V$_2$O$_5$·H$_2$O were hydrothermally synthesized for divalent metals of M = Mg, Co, Ni in addition to the first-reported M = Zn compound. The σ-type structures, consisting of V$_2$O$_5$ layers with three octahedral and one tetrahedral V atoms and interlayer M(H$_2$O)$_4$ rectangles, were confirmed by single-crystal X-ray diffractometry. The Ni compound crystallizes in the same $P\bar{1}$ phase as the Zn compound while the Mg and Co compounds crystallize in the new $P2_1/a$ phase of higher symmetry. The $P2_1/a$ phases is an undistorted form of the $P\bar{1}$ phases, where the distortion is caused by the locations of interlayer water molecules. Among four V atoms one octahedral atom is tetravalent and others are pentavalent, being consistent with the average V$^{4.75+}$ valence. The M(H$_2$O)$_4$ is held by two apical oxygens of VO$_4$ tetrahedra to form a regular MO$_6$ octahedron and thus M^{2+} ions must fit for the octahedral oxygen coordination. © 1999 Academic Press

INTRODUCTION

In the vanadium oxide bronzes (VOB), there is a group of layered phases consisting of V–O layered frameworks and interlayer M atoms (1). Major phases of the group are listed such as α type (α-M_xV$_2$O$_5$ ($x \approx 0$) (2) or α'-M_xV$_2$O$_5$ ($x \approx 1$) (3)), δ type (δ-M_xV$_2$O$_5$) (4), and γ type (γ-M_{1+x}V$_3$O$_8$) (5). Their V–O layered frameworks are made up with linkages of edge-sharing VO$_6$ octahedra and/or VO$_5$ trigonal bipyramids. The interlayer M atoms are bonded to apical oxygens of VO$_6$ and/or VO$_5$ polyhedra. Recently, utilizing hydrothermal synthesis we have added a new member in the group that is called σ type and formulated by $M_{0.25}$V$_2$O$_5$·H$_2$O (6). The first σ-type phase was σ-Zn$_{0.25}$V$_2$O$_5$·H$_2$O synthesized from ZnCl$_2$ and VO(OH)$_2$. In spite of poor quality of the single crystal the σ-type structure has been clearly demonstrated; the V–O framework consists of the linkage of edge-sharing VO$_6$ octahedra

and VO$_5$ trigonal bipyramids and vertex-sharing VO$_4$ tetrahedra. The interlayer Zn atom forms a Zn(H$_2$O)$_4$ rectangle and is bonded to two apical oxygens of the VO$_4$ tetrahedra on opposite sides, resulting in a ZnO$_6$ regular octahedron. However, more precise structural information should be needed to discuss, for example, crystal systems, lattice distortions, locations of interlayer species, and valence states of V atoms. In the present study, single crystals of σ-type phases were hydrothermally grown for a series of divalent metals of M = Mg, Mn, Co, Ni, which provide us full structural information and a criterion of the σ-type phase formation.

EXPERIMENTAL

Sample Preparation

Samples of σ-$M_{0.25}$V$_2$O$_5$·H$_2$O phases were synthesized using hydrothermal methods as follows. Starting materials were sealed in Pyrex ampules followed by hydrothermal treatment in an autoclave at 280°C for 30–48 h. Products were separated by filtration, washed with distilled water and dried at 50°C. For M = Mg, monophasic powder samples were obtained from a suspension of VO(OH)$_2$ powders in a MgSO$_4$ solution and single crystals were grown from a mixed solution of NaVO$_3$ and MgI$_2$. For M = Mn, Co, Ni, single crystals were separated from hydrothermal products obtained from MCl$_2$–VOCl$_2$ mixed solutions: the products contained mainly green fibrous powders of hydrous σ-type phases δ-M_xV$_2$O$_5$·nH$_2$O ($x \approx 0.15$, $n \approx 2$–3) with layer spacings 13.4–13.8 Å (6). The final pH values of the solutions were 3.0–3.3 for VO(OH)$_2$–MgSO$_4$, 5.5–5.8 for NaVO$_3$–MgI$_2$, and 2.5–3.0 for MCl$_2$–VOCl$_2$. All the crystals have a common rhomboid shape with black color. Full chemical analysis was made on the Mg compound by thermogravimetry for water contents, atomic absorptiometry for Mg contents, light absorptiometry for V contents/valences, and energy dispersive X-ray spectroscopy for Mg/V atomic ratios, giving the composition of Mg$_{0.25(1)}$V$_2$O$_5$·0.98(5)H$_2$O. For M = Mn, Co, Ni, syntheses of monophasic

samples were unsuccessful and thus only M/V atomic ratios of 0.125 were confirmed by energy dispersive X-ray spectroscopy.

Single-Crystal X-Ray Diffraction

Single-crystal X-ray diffraction measurements were performed on crystals of all the M compounds whose crystalline phases were confirmed to be the σ phase by Weissenberg camera work. Crystals suitable for the X-ray diffraction study were selected with effort since most crystals gave somewhat elongated diffraction spots in Weissenberg photographs. Selected crystals were mounted on a Rigaku AFC-7R diffractometer with monochromatized MoKα radiation. Data were collected by the ω–2θ scanning method, and no significant intensity fluctuations were detected by monitoring three standard reflections every 150 data. Empirical absorption corrections of the ψ scan method were applied and reflections with intensities $I > 3\sigma(I)$ were used in structure refinements. Data processing and structure refinement calculations were performed using the TEXSAN software package (7). Experimental conditions and crystallographic data are listed in Table 1. The results for the Mn compound are excluded in Table 1 because its structure refinement was not satisfactory, and only the unit cell parameters are given here: the monoclinic system $P2_1/a$ with $a = 10.608(3)$ Å, $b = 8.026(2)$ Å, $c = 10.814(2)$ Å, and $\beta = 91.34(3)°$.

Structure Determination

In the previous study (6), the space group of σ-$Zn_{0.25}V_2O_5 \cdot H_2O$ was determined to be $P\bar{1}$ but it was then discussed that the σ phase should exhibit the space group $P2_1/a$ as well. The crystal systems were thus carefully examined and were confirmed to be monoclinic ($P2_1/a$) for $M = $ Mg, Co, (Mn) and triclinic ($P\bar{1}$) for $M = $ Ni. Atomic coordinates derived from those of σ-$Zn_{0.25}V_2O_5 \cdot H_2O$ (6) were successfully utilized for both space groups as initial models. Structure refinements using anisotropic temperature factors converged to the R values given in Table 1. Site occupancies of M atoms were refined to 1.036(18) for Mg (then fixed to 1), 0.964(4) for Co, 0.992(6) for Ni(1), and 0.988(6) for Ni(2), indicating that all the M sites are practically fully occupied. Atomic coordinates and equivalent temperature factors are listed in Table 2.

TABLE 1
Crystallographic and Experimental Parameters of
σ-$M_{0.25}V_2O_5 \cdot H_2O$ for $M = $ Mg, Co, Ni

	Mg	Co	Ni
Space group	$P2_1/a$	$P2_1/a$	$P\bar{1}$
a (Å)	10.625(6)	10.616(3)	10.615(1)
b (Å)	8.045(7)	8.028(3)	8.0312(8)
c (Å)	10.771(7)	10.732(5)	10.6964(9)
α (deg)	90	90	90.70(1)
β (deg)	91.23(5)	91.40(3)	91.223(8)
γ (deg)	90	90	90.093(8)
Z	8	8	8
Crystal size (mm)	$0.20 \times 0.15 \times 0.01$	$0.30 \times 0.25 \times 0.01$	$0.30 \times 0.20 \times 0.01$
$2\theta_{max}$ (deg)	70	70	80
Scan width, $\Delta\omega$ (deg)	$1.78 + 0.30 \tan\theta$	$1.78 + 0.30 \tan\theta$	$1.78 + 0.30 \tan\theta$
μ (MoKα) (cm^{-1})	40.30	47.22	50.35
Trans. coeff. min/max	0.825/1.000	0.500/1.000	0.415/1.000
No. of reflections ($I > 0$)	3618	4005	10445
No. of reflections ($I > 3(I)$)	2014	2613	6150
R_{int}	0.029	0.020	0.024
No. of variables	151	152	304
R/R_w	0.056/0.067	0.049/0.041	0.062/0.072

TABLE 2
Atomic Coordinates and Equivalent Temperature Factors of
σ-$M_{0.25}V_2O_5 \cdot H_2O$ for $M = $ Mg, Ni, Co

Atom	x	y	z	B_{eq} (Å^2)
		$M = $ Mg		
Mg	0	0.5	0.5	1.60(8)
V(1)	0.7018(1)	0.7173(2)	0.1409(1)	0.89(2)
V(2)	0.6871(1)	0.3394(2)	0.1419(1)	0.77(2)
V(3)	0.9166(1)	0.0389(2)	0.1390(1)	0.76(2)
V(4)	0.4749(1)	0.0314(2)	0.1613(1)	0.71(2)
O(1)	0.8136(4)	0.5185(6)	0.1231(4)	0.81(8)
O(2)	0.5802(4)	0.5374(7)	0.1081(5)	0.96(8)
O(3)	0.7889(5)	0.1921(7)	0.0800(5)	1.01(9)
O(4)	0.5256(4)	0.2405(6)	0.1214(5)	0.90(9)
O(5)	0.8316(5)	0.8665(6)	0.0898(5)	1.05(9)
O(6)	0.5712(5)	0.8917(7)	0.1017(5)	1.11(9)
O(7)	0.7069(6)	0.7343(8)	0.2904(6)	1.7(1)
O(8)	0.7026(5)	0.3174(8)	0.2885(5)	1.6(1)
O(9)	0.9039(5)	0.0374(8)	0.2868(5)	1.6(1)
O(10)	0.4892(5)	0.0167(8)	0.3120(5)	1.7(1)
O$_w$(1)	0.002(1)	0.761(1)	0.4897(9)	7.3(3)
O$_w$(2)	0.8064(7)	0.509(2)	0.5083(7)	6.6(3)
		$M = $ Co		
Co	0	0.5	0.5	2.01(3)
V(1)	0.70256(9)	0.7178(1)	0.1420(1)	0.75(2)
V(2)	0.68763(8)	0.3404(1)	0.1421(1)	0.79(2)
V(3)	0.91687(8)	0.0395(1)	0.13939(9)	0.75(2)
V(4)	0.47567(8)	0.0317(1)	0.16165(9)	0.66(2)
O(1)	0.8139(3)	0.5194(5)	0.1220(3)	0.70(7)
O(2)	0.5808(3)	0.5370(5)	0.1087(4)	0.87(7)
O(3)	0.7896(3)	0.1922(5)	0.0803(4)	1.01(8)
O(4)	0.5253(3)	0.2403(5)	0.1193(4)	0.82(7)
O(5)	0.8324(3)	0.8667(5)	0.0904(4)	0.99(8)
O(6)	0.5726(3)	0.8909(5)	0.1016(4)	1.05(8)
O(7)	0.7076(4)	0.7366(6)	0.2914(4)	1.5(1)
O(8)	0.7037(4)	0.3186(6)	0.2901(4)	1.5(1)
O(9)	0.9039(4)	0.0407(6)	0.2869(4)	1.68(9)
O(10)	0.4903(4)	0.0185(6)	0.3138(4)	1.54(9)
O$_w$(1)	0.005(1)	0.7579(7)	0.4878(8)	8.1(2)
O$_w$(2)	0.8085(4)	0.505(1)	0.5096(5)	6.6(2)

TABLE 2—*Continued*

Atom	x	y	z	B_{eq} (Å²)
		M = Ni		
Ni(1)	0	0.5	0.5	1.57(4)
Ni(2)	0.5	0	0.5	1.66(4)
V(1)	0.7023(1)	0.7203(2)	0.1423(1)	0.67(2)
V(2)	0.6868(1)	0.3425(2)	0.1434(1)	0.65(2)
V(3)	0.9166(1)	0.0418(2)	0.1388(1)	0.64(2)
V(4)	0.4754(1)	0.0336(2)	0.1632(1)	0.62(2)
V(5)	0.2025(1)	0.7840(2)	0.1425(1)	0.66(2)
V(6)	0.1871(1)	0.1620(2)	0.1412(1)	0.65(2)
V(7)	0.4164(1)	0.4624(2)	0.1402(1)	0.69(2)
V(8)	0.9753(1)	0.4694(2)	0.1624(1)	0.60(2)
O(1)	0.8149(5)	0.5191(6)	0.1247(5)	0.65(9)
O(2)	0.5794(5)	0.5406(6)	0.1091(6)	0.9(1)
O(3)	0.7885(5)	0.1947(7)	0.0809(6)	0.9(1)
O(4)	0.5260(5)	0.2397(6)	0.1241(5)	0.73(9)
O(5)	0.8315(5)	0.8678(6)	0.0911(5)	0.77(9)
O(6)	0.5736(5)	0.8909(7)	0.1031(6)	1.0(1)
O(7)	0.3145(5)	0.9817(6)	0.1243(5)	0.67(9)
O(8)	0.0802(5)	0.9637(6)	0.1077(5)	0.79(9)
O(9)	0.2884(5)	0.3097(6)	0.0805(6)	0.9(1)
O(10)	0.0261(5)	0.2596(6)	0.1198(5)	0.76(9)
O(11)	0.3330(5)	0.6348(6)	0.0922(6)	1.0(1)
O(12)	0.0720(6)	0.6108(7)	0.1032(6)	1.0(1)
O(13)	0.7067(6)	0.7426(8)	0.2920(6)	1.5(1)
O(14)	0.7022(6)	0.3228(7)	0.2906(6)	1.3(1)
O(15)	0.9042(6)	0.0462(8)	0.2872(6)	1.4(1)
O(16)	0.4885(6)	0.0231(8)	0.3141(6)	1.5(1)
O(17)	0.2064(7)	0.7681(8)	0.2899(6)	1.5(1)
O(18)	0.2027(7)	0.1859(8)	0.2885(6)	1.4(1)
O(19)	0.4017(7)	0.4642(8)	0.2877(6)	1.4(1)
O(20)	0.9897(8)	0.4829(8)	0.3155(6)	1.5(1)
O$_w$(1)	0.0321(9)	0.7519(9)	0.4897(7)	3.3(2)
O$_w$(2)	0.8081(7)	0.539(1)	0.5071(7)	3.2(2)
O$_w$(3)	0.528(1)	0.252(1)	0.5149(8)	4.3(2)
O$_w$(4)	0.3081(7)	0.021(1)	0.5101(7)	3.3(2)

RESULTS AND DISCUSSION

Framework Structures of V_2O_5 Layers

The structure of σ phase has already been described in the previous paper for triclinic σ-$Zn_{0.25}V_2O_5 \cdot H_2O$ (6); however, the structural information was rather limited because of the poor quality of the crystal. In the present study, we have obtained much more improved structural data and more importantly disclosed the monoclinic option whose existence had been suggested. The new results enable us to provide a detailed structural discussion on the σ phase.

The monoclinic structure of σ phase is depicted in Fig. 1 for σ-$Co_{0.25}V_2O_5 \cdot H_2O$, which is essentially the same as the triclinic structure of σ-$Ni_{0.25}V_2O_5 \cdot H_2O$. The structure adopts a layered type consisting of V_2O_5 layers and interlayer hydrous M atoms. The V_2O_5 layer exhibits a framework of V–O polyhedra of four kinds: three octahedra of V(1)O_6, V(2)O_6, and V(3)O_6 and one tetrahedron of V(4)O_4 for

which V–O distances are listed in Table 3. It is noted for the $P\bar{1}$ symmetry that V(5), V(6), V(7), and V(8) become equivalent with V(1), V(2), V(3), and V(4), respectively, in the $P2_1/a$ symmetry. As indicated previously (6) the V(3)–O coordinations may be regarded as VO$_5$ trigonal bipyramids without V(3)–O(2) bonds that show rather long distances of 2.637–2.667 Å (Table 3) but here we group them into VO$_6$ octahedra for simplicity. Figure 2 depicts the polyhedral structure unit of which the V_2O_5 layers is built, namely, edge-sharing VO$_6$ octahedra to which VO$_4$ tetrahedra are connected by vertex sharing. Bond valence calculations (8) are made for the V–O polyhedra and the results are given in Table 4. Interestingly valence states of V atoms are clearly differentiated as V^{4+} for V(1) and V^{5+} for V(2), V(3), and V(4), being consistent with the average valence of 4.75 for the $M_{0.25}V_2O_5$ formula. It is no wonder that tetrahedral V(4) is pentavalent. Octahedral $V^{IV, V}$ atoms have shortest

TABLE 3
V–O Bond Distances (Å) of V–O Polyhedra
in σ-$M_{0.25}V_2O_5 \cdot H_2O$ for M = Mg, Co, Ni

M = Mg, Co			M = Ni			
	Mg	Co				
V(1)O$_6$			V(1)O$_6$		V(5)O$_6$	
V(1)–O(1)	2.004(5)	1.998(4)	V(1)–O(1)	2.020(5)	V(5)–O(7)	1.996(5)
V(1)–O(2)	1.967(5)	1.970(4)	V(1)–O(2)	1.968(5)	V(5)–O(8)	1.976(5)
V(1)–O(3)^a	2.392(6)	2.397(5)	V(1)–O(9)^f	2.397(6)	V(5)–O(3)^f	2.402(6)
V(1)–O(5)	1.918(5)	1.916(4)	V(1)–O(5)	1.904(5)	V(5)–O(11)	1.914(5)
V(1)–O(6)	2.012(5)	1.998(4)	V(1)–O(6)	1.979(6)	V(5)–O(12)	1.996(6)
V(1)–O(7)	1.616(6)	1.610(5)	V(1)–O(13)	1.609(7)	V(5)–O(17)	1.583(7)
V(2)O$_6$			V(2)O$_6$		V(6)O$_6$	
V(2)–O(1)	1.983(5)	1.981(4)	V(2)–O(1)	1.978(5)	V(6)–O(7)^i	1.993(5)
V(2)–O(2)	1.986(5)	1.971(5)	V(2)–O(2)	1.992(5)	V(6)–O(8)^i	1.978(6)
V(2)–O(3)	1.746(5)	1.749(4)	V(2)–O(3)	1.743(6)	V(6)–O(9)	1.741(5)
V(2)–O(4)	1.901(5)	1.912(4)	V(2)–O(4)	1.902(5)	V(6)–O(10)	1.892(5)
V(2)–O(5)^b	2.509(6)	2.507(5)	V(2)–O(11)^f	2.534(6)	V(6)–O(5)^f	2.498(6)
V(2)–O(8)	1.594(6)	1.603(5)	V(2)–O(14)	1.589(6)	V(6)–O(18)	1.590(7)
V(3)O$_6$			V(3)O$_6$		V(7)O$_6$	
V(3)–O(2)^c	1.880(5)	1.883(4)	V(3)–O(8)^g	1.882(6)	V(7)–O(2)	1.887(5)
V(3)–O(2)b	2.662(6)	2.661(4)	V(3)–O(8)^f	2.637(6)	V(7)–O(2)^f	2.667(6)
V(3)–O(3)	1.930(5)	1.921(4)	V(3)–O(3)	1.930(6)	V(7)–O(9)	1.923(5)
V(3)–O(4)^c	2.130(5)	2.123(5)	V(3)–O(10)^h	2.113(5)	V(7)–O(4)	2.142(5)
V(3)–O(5)^d	1.732(6)	1.726(4)	V(3)–O(5)^i	1.729(5)	V(7)–O(11)	1.722(5)
V(3)–O(9)	1.600(6)	1.593(4)	V(3)–O(15)	1.596(7)	V(7)–O(19)	1.589(6)
V(4)O$_4$			V(4)O$_4$		V(8)O$_4$	
V(4)–O(1)^e	1.799(5)	1.808(4)	V(4)–O(7)^i	1.796(5)	V(8)–O(1)	1.788(5)
V(4)–O(4)	1.821(5)	1.816(5)	V(4)–O(4)	1.796(5)	V(8)–O(10)^h	1.826(5)
V(4)–O(6)^d	1.659(5)	1.668(4)	V(4)–O(6)^i	1.682(6)	V(8)–O(12)^h	1.670(6)
V(4)–O(10)	1.631(6)	1.640(4)	V(4)–O(16)	1.620(7)	V(8)–O(20)	1.644(7)

Note. Symmetry codes are as follows: $^a \frac{3}{2} - x, \frac{1}{2} + y, -z$; $^b \frac{3}{2} - x, y - \frac{1}{2}, -z$; $^c x + \frac{1}{2}, \frac{1}{2} - y, z$; $^d x, y - 1, z$; $^e x - \frac{1}{2}, \frac{1}{2} - y, z$; $^f 1 - x, 1 - y, -z$; $^g x + 1, 1 - y, z$; $^h x + 1, y, z$; $^i x, 1 - y, z$.
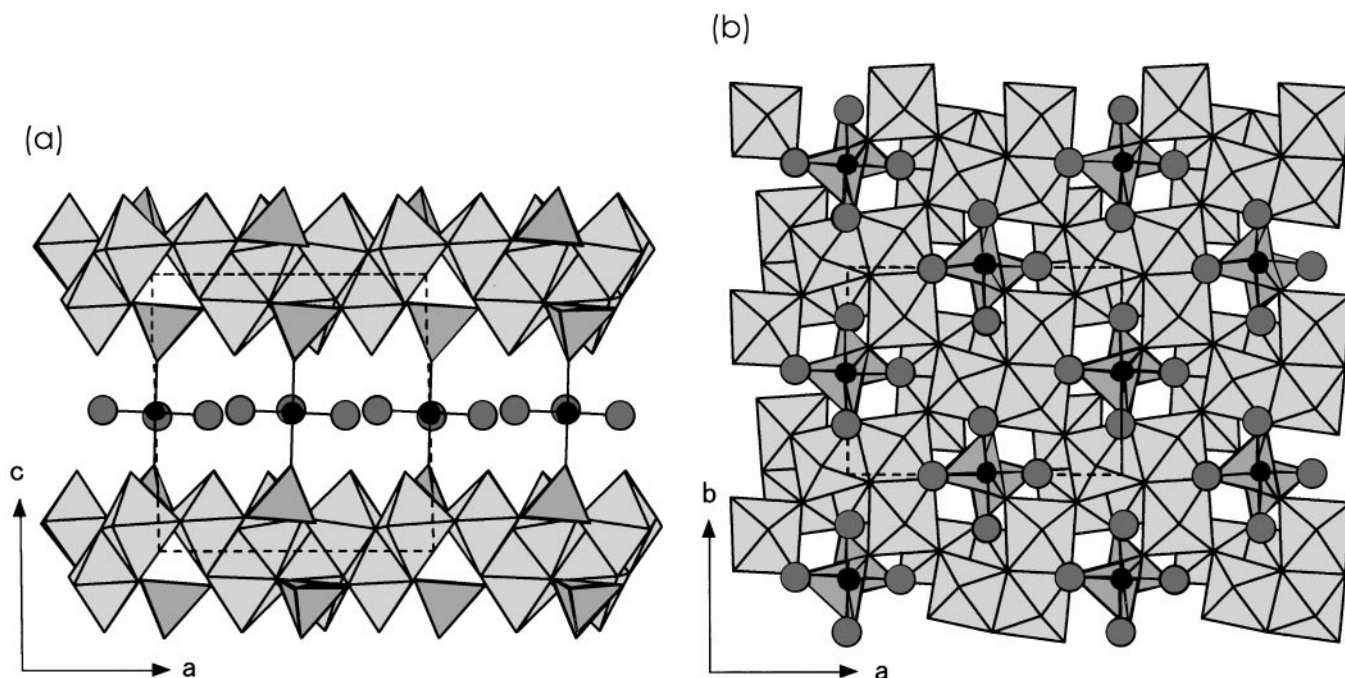
FIG. 1. Crystal structure of σ-$M_{0.25}V_2O_5 \cdot H_2O$ (M = Co) with the $P2_1/a$ symmetry projected onto (a) the ac plane and (b) the ab plane. V_2O_5 layers are represented by VO_6 octahedra (light-shaded) and VO_4 tetrahedra (dark-shaded), and small and large circles denote M and O_w atoms, respectively.
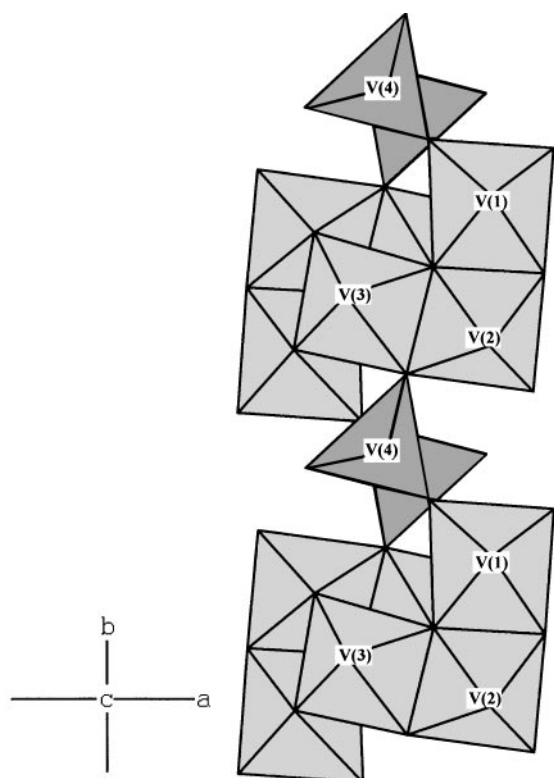

FIG. 2. V–O polyhedral structure units of the V_2O_5 layer of σ-$M_{0.25}V_2O_5 \cdot H_2O$. V(1), V(2), and V(3) form VO_6 octahedra and V(4) form VO_4 tetrahedra.

V–O distances of 1.6 Å with apical oxygens (V(1)–O(7), V(2)–O(8), V(3)–O(9)) and on the opposite side longest V–O distances of 2.4 to 2.7 Å (V(1)–O(3), V(2)–O(5), V(3)–O(2)). Among the longest V–O distances, V(1)–O(3) shows a relatively shorter distance of 2.392–2.402 Å, indicating that V^{IV} takes less deformed VO_6 octahedron as compared to that for V^V. Similar site preference of V^{IV} over octahedral sites was observed in other layered bronze of δ-$Sr_{0.5}V_2O_5$ (9).

TABLE 4
Bond Valence Sums of V in σ-$M_{0.25}V_2O_5 \cdot H_2O$ for
M = Mg, Co, Ni

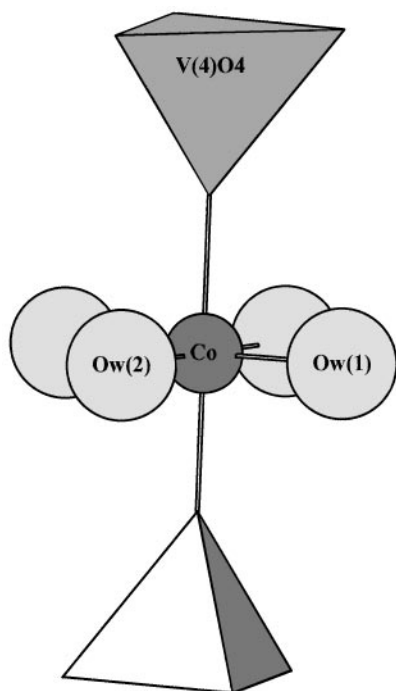|	Mg		Co			Ni	
	V^{IV}	V^V	V^{IV}	V^V		V^{IV}	V^V
V(1)	4.09	4.36	4.15	4.41	V(1)	4.17	4.45
					V(5)	4.29	4.57
V(2)	4.76	5.05	4.70	5.00	V(2)	4.78	5.08
					V(6)	4.81	5.11
V(3)	4.68	4.97	4.76	5.05	V(3)	4.73	5.02
					V(7)	4.78	5.08
V(4)	4.71	4.99	4.62	4.89	V(4)	4.74	5.02
					V(8)	4.62	4.89

FIG. 3. Octahedral oxygen coordination of interlayer M atom (M = Co) with two apical oxygens of $V(4)O_4$ tetrahedra and four water molecules (O_w atoms).

TABLE 6
Anisotropic Displacement Parameters of M and O_w for M = Mg, Co, Ni

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
			M = Mg			
Mg	0.025(2)	0.024(2)	0.012(2)	−0.001(2)	−0.001(1)	0.000(1)
$O_w(1)$	0.22(1)	0.023(4)	0.029(5)	−0.008(6)	0.016(6)	−0.002(4)
$O_w(2)$	0.028(4)	0.20(1)	0.020(3)	0.005(6)	−0.002(3)	−0.007(6)
			M = Co			
Co	0.0303(8)	0.032(1)	0.0145(7)	−0.0034(6)	0.0014(5)	−0.0019(6)
$O_w(1)$	0.248(9)	0.017(3)	0.043(5)	−0.003(5)	0.034(5)	−0.000(3)
$O_w(2)$	0.026(3)	0.201(9)	0.024(3)	0.005(5)	0.000(3)	−0.009(6)
			M = Ni			
Ni(1)	0.029(1)	0.0226(9)	0.0087(8)	0.0005(7)	0.0007(7)	−0.0001(6)
Ni(2)	0.027(1)	0.029(1)	0.0077(8)	0.0028(7)	−0.0009(7)	0.0023(6)
$O_w(1)$	0.085(7)	0.025(4)	0.016(4)	−0.007(4)	0.014(4)	−0.004(3)
$O_w(2)$	0.028(4)	0.078(6)	0.014(4)	0.010(4)	−0.001(3)	−0.006(4)
$O_w(3)$	0.110(9)	0.030(4)	0.022(5)	−0.016(5)	0.003(5)	−0.001(4)
$O_w(4)$	0.028(4)	0.082(7)	0.014(4)	0.004(4)	−0.004(3)	−0.004(4)

Distribution of Interlayer Atoms and Lattice Distortion

Interlayer M atoms take regular octahedral oxygen coordinations as depicted in Fig. 3. The MO_6 octahedron is composed of two apical oxygens of VO_4 tetrahedra on opposite sides and four water molecules (denoted by O_w) in a planar rectangle coordination (MO_{w4} rectangle) with M–O distances listed in Table 5. The MO_{w4} rectangle units are regarded as hydrous $[M(H_2O)_4]^{2+}$ ions on an ionic basis. We discussed in the previous paper (6) based solely on the $P\bar{1}$ structure of the Zn compound that the $P\bar{1}$ structure

TABLE 5
M–O Bond Distances in MO_6 Octahedra for M = Mg, Co, Ni

		M = Mg			
Mg–O(10)^{a,b}	2.035(5)	Mg–$O_w(1)^{c,d}$	2.100(9)	Mg–$O_w(2)^{e,f}$	2.062(8)
		M = Co			
Co–O(10)^{a,b}	2.003(4)	Co–$O_w(1)^{c,d}$	2.074(7)	Co–$O_w(2)^{e,f}$	2.040(5)
		M = Ni			
Ni(1)–O(20)^{g,f}	2.035(5)	Ni(1)–$O_w(1)^{c,d}$	2.056(7)	Ni(1)–$O_w(2)^{g,f}$	2.064(8)
Ni(2)–O(16)^{c,h}	2.001(5)	Ni(2)–$O_w(3)^{c,h}$	2.051(7)	Ni(2)–$O_w(4)^{c,h}$	2.050(8)

Note. Symmetry codes are as follows: $^a x - \frac{1}{2}, \frac{1}{2} - y, z$; $^b \frac{1}{2} - x, y + \frac{1}{2}, 1 - z$; $^c x, y, z$; $^d - x, 1 - y, 1 - z$; $^e 1 - x, y, z$; $^f 1 - x, 1 - y, 1 - z$; $^g x - 1, y, z$; $^h 1 - x, - y, 1 - z$

was probably a distorted form of the $P2_1/a$ structure and O_w atoms were responsible for the distortion. Now we have succeeded in synthesizing the σ phase of $P2_1/a$ type whose structural characterization provides us significant information regarding the lattice distortion. Table 6 lists anisotropic displacement parameters (U_{ij}) for M and O_w atoms and Fig. 4 compares thermal ellipsoids of MO_{w4} rectangles between the $P2_1/a$ and the $P\bar{1}$ structures. As pointed out previously (6) O_w atoms prefer the $P\bar{1}$ positions (Fig. 4a) where MO_{w4} units cooperatively rotate around the c^* axis by $\sim 7°$. However, the V_2O_5 layer does exhibit the $P2_1/a$ symmetry in principle but the M atom positions match both symmetries. Therefore the space group is determined as a result of the competition between the symmetries of the V_2O_5 layer ($P2_1/a$) and the O_w positions ($P\bar{1}$). When the former overcomes the latter, the space group $P2_1/a$ results (Fig. 4b). In this case the MO_{w4} rectangles are located almost parallel to the a or b axis ($x \approx 0$ for $O_w(1)$, $y \approx 0.5$ for $O_w(2)$) to avoid closer contact between O_w atoms of adjacent MO_{w4} rectangles since O_w atoms come closer as x of $O_w(1)$ and y of $O_w(2)$ deviate from 0 and 0.5, respectively. As seen in Table 6 and Fig. 4, the anisotropic displacement parameters of O_w atoms in the $P2_1/a$ symmetry are substantially larger than those in the $P\bar{1}$ symmetry especially for U_{11} of $O_w(1)$ and U_{22} of $O_w(2)$. It is said that O_w atoms in the $P2_1/a$ symmetry show large positional fluctuations which eventually lead to the distortion into the $P\bar{1}$ symmetry in which the fluctuations become smaller. The $P2_1/a$ structure is adopted by M = Mg, Co, (Mn) and the $P\bar{1}$ structure by M = Ni, Zn. The lattice distortion is not related to M^{2+} ion sizes nor to M–O_w or M–O distances.
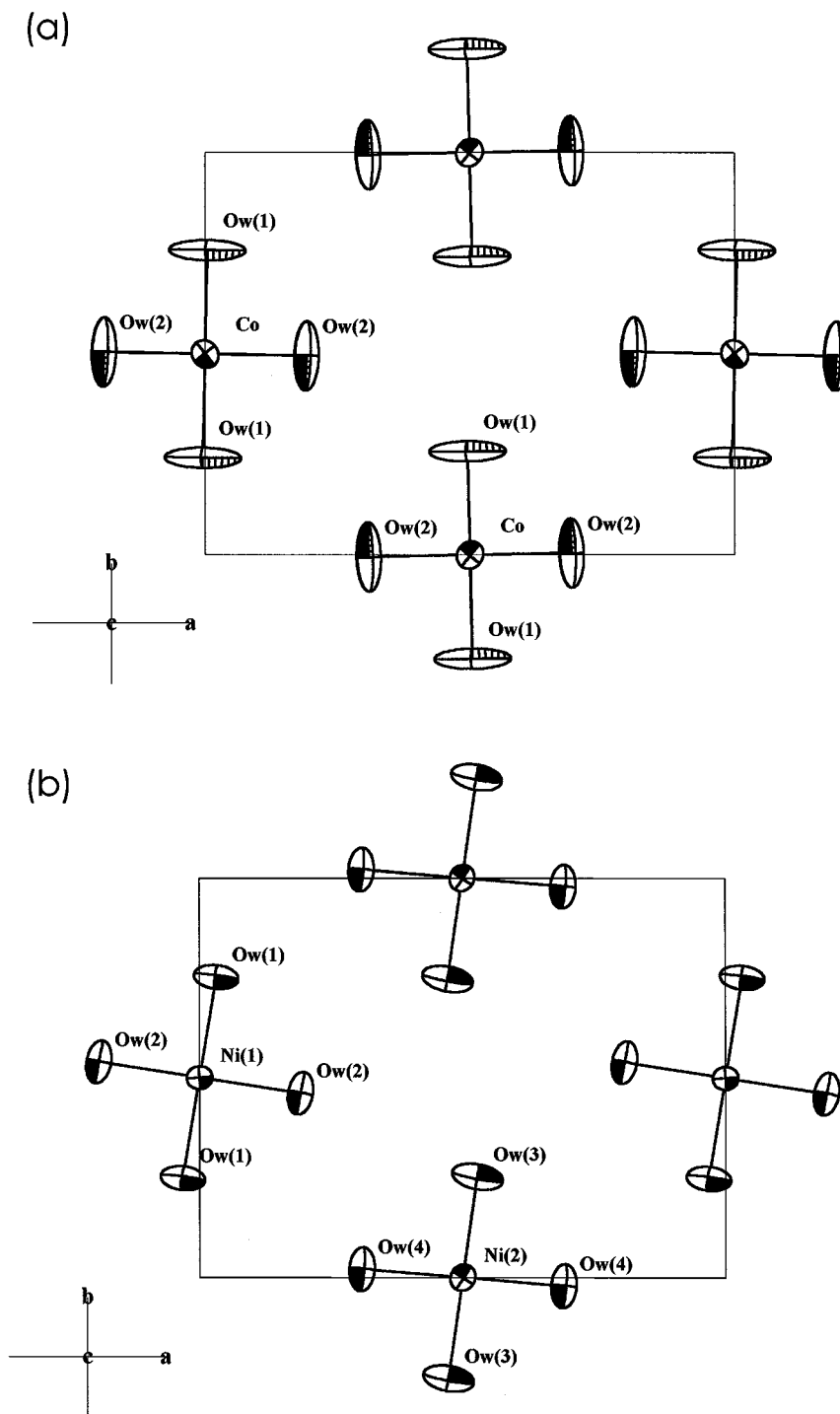
FIG. 4. Thermal ellipsoids of MO_{w4} rectangles for (a) the $P2_1/a$ symmetry (M = Co) and (b) the $P\bar{1}$ symmetry (M = Ni). Ellipsoids are drawn with 50% probabilities.

Though the exact reason is unclear, it seems that the distortion occurs in M of larger atomic numbers.

The σ phase is adopted by M = Mg, Mn, Co, Ni, Zn, i.e., divalent cations with ionic radii (10) ranging from 0.69 Å (Ni^{2+}) to 0.83 Å (Mn^{2+}). For larger divalent M atoms such

as Ca and Sr, attempts to synthesize the σ phase have been unsuccessful. This is a great difference between the σ phase and the corresponding layered hydrous δ phase that is formulated identically by $M_{0.25}V_2O_5 \cdot H_2O$ (11). The δ phase can offer 6- and 7-coordination sites for interlayer

M atoms while the σ phase offers solely octahedral sites because apical oxygens of only VO_4 tetrahedra are bonded to M atoms. For example, $M = Ni$ that prefers a 6-coordination site forms both δ- and σ-$Ni_{0.25}V_2O_5 \cdot H_2O$ while $M = Ca$ that prefers a 7-coordination site forms only δ-$Ca_{0.25}V_2O_5 \cdot H_2O$ (11). Therefore the sizes of M atoms which can form the σ phase are limited to the above range where octahedral coordination is adopted.

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