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Crystal Structure and Metal Distribution of α-CoV_3O_8

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Single crystals of α-CoV_3O_8, a mixed-valence compound of $V^{IV/V}$, were hydrothermally synthesized. It crystallizes in the orthorhombic system *Ibam* with $a = 14.3298(6)$ Å, $b = 9.8906(6)$ Å, $c = 8.3950(8)$ Å, and $Z = 8$. The structure was refined to $R = 0.034$ and $R_w = 0.030$ for 1558 reflections with $I > 3\sigma(I)$. There are three kinds of metal sites, namely, octahedral *M* (16 *k*) for *M* = Co, V(1), tetrahedral V(2) (8*j*), and trigonal-bipyramidal V(3) (8*j*), where the *M* site was found to consist of half-occupied Co and V(1). Its polyhedral framework is built up of MO_6 slabs and $V(2)O_4$–$V(3)O_5$ units. The MO_6 slab is constructed by linking zigzag chains of edge-sharing MO_6 octahedra running along the *c* axis. The linkage is made along the *b* axis by sharing common vertices of O(5) and thus the slab stands in the bc plane. The $V(2)O_4$–$V(3)O_5$ unit, playing a role in bridging MO_6 slabs, is made of an edge-sharing $V(3)O_5$ pair to which two $V(2)O_4$ are attached. Valence states of metals were evaluated as Co^{II}, $V(1)^{IV}$, $V(2)^{V}$, and $V(3)^{V}$. The metal distribution over the *M* site is basically random but is constrained by a rule to form a Co–O(5)–V(1) group at the linkage of MO_6 chains, which accounts for the half-occupancies of Co and V(1) as well as a positional shift of O(5). The structure is compared with those of α-ZnV_3O_8 and β-MgV_3O_8 in particular reference to metal distributions. The magnetic susceptibility curve of α-CoV_3O_8 exhibits a sharp peak at 8 K, suggesting the onset of antiferromagnetic order. © 1998 Academic Press

INTRODUCTION

There are various phases of mixed-valence vanadium (IV, V) oxides in ternary systems *M*–V–O with foreign *M* metals. A major part of them, especially for *M* = alkali or alkaline-earth metals, are known as the vanadium oxide bronzes (VOB), which have been attracting much attention because of their structural and physical properties (1). VOBs have general structures consisting of V–O polyhedral frameworks and interstitial foreign metals. On the other hand, phases with *M* = 3*d* transition metals are expected to exhibit framework structures made up of both V–O and *M*–O polyhedra. However, only a few *M*–V–O compounds of this class are known. For example, in the CoO–VO_2–V_2O_5 system there is only one definite mixed-valence compound, CoV_3O_8, originally formulated as $Co_{1+y}(V_3O_8)_2$ ($0.90 \leq y \leq 1$) (2). This is also the case for the NiO–VO_2–V_2O_5 system (2). CoV_3O_8 was reported to adopt the α form below 650°C and transforms reversibly into a high-temperature phase of the β form; the α form crystallizes in the body-centered orthorhombic system *Ic*2*a* or *Icma* with cell parameters $a = 14.234(10)$ Å, $b = 8.390(8)$ Å, and $c = 9.822(9)$ Å and the β form crystallizes in the *C*-centered monoclinic system with $a = 10.297(9)$Å, $b = 8.524(7)$ Å, $c = 7.774(9)$ Å, and $\beta = 119.1(4)^\circ$ (2). Isomorphous phases were found for other divalent metals of *M* = Ni, Zn, and Mg: MgV_3O_8 and ZnV_3O_8 exhibit both the α and β forms (2, 3) whereas NiV_3O_8 exhibits the α form and an undefined β form (2). Though the structures of α- and β-CoV_3O_8 remain unknown, those of α-ZnV_3O_8 (4) and β-MgV_3O_8 (5) have been determined and both phases adopt similar framework structures consisting of MO_6 octahedra and V–O polyhedra. Thus, in these mixed-valence MV_3O_8 phases, in contrast to the VBO phases, both *M* and V metals construct polyhedral frameworks. Further insight into the crystal chemistry of the MV_3O_8 phases should be of interest.

In the present study single crystals of α-CoV_3O_8 have been hydrothermally grown and its structure has been solved. The structure is closely related to that of α-ZnV_3O_8 but has a different metal distribution as well as a different space group; this point is discussed together with the structure of β-MgV_3O_8. The magnetic susceptibility measurement suggested antiferromagnetic order below 8.2 K.

EXPERIMENTAL

Sample Preparation

Starting materials for V and Co sources were $VO(OH)_2$ powders and CoI_2 or $CoCl_2$ aqueous solutions. $VO(OH)_2$ powders were prepared in advance by the hydrothermal treatment of a mixture of $VOSO_4$ and NaOH solutions at 150°C. A suspension of $VO(OH)_2$ powders (0.5 g) in a CoI_2 or $CoCl_2$ solution (80 ml, 0.1 $mol l^{-1}$) was sealed in a Pyrex

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ampoule and treated hydrothermally in an autoclave at 280°C for 48 h. Precipitates were separated by filtration and washed thoroughly with distilled water and ethanol. The products consisted of shiny black granules and black-brown powders. The black granules were easily separated by repeated decantation and sonication and appeared to be single-crystalline particles under an optical microscope. The crystalline phase was identified as α-CoV_3O_8 (2) by powder X-ray diffractometry. The Co/V atomic ratio was obtained to be 0.333(2) by energy-dispersive X-ray analysis. The by-product of the black-brown powders was found to be the $VO_2(A)$ phase (6). A magnetic susceptibility measurement was carried out on as-synthesized CoV_3O_8 granules by using a SQUID magnetometer from 5 to 300 K under a magnetic field of 1000 G.

TABLE 1
Crystallographic Data and Experimental Parameters for α-CoV_3O_8

Space group	*Ibam*
a (Å)	14.3298(6)
b (Å)	9.8906(6)
c (Å)	8.3950(8)
V (Å^3)	1189.8(1)
Z	8
D_c (g cm^{-3})	3.794
μ (cm^{-1})	71.70
Number of reflections ($I > 0$)	2072
Number of reflections ($I > 3\sigma(I)$)	1558
Number of variables	67
R	0.034
R_w	0.030

Single-Crystal X-Ray Diffraction Study

A single crystal of CoV_3O_8 with dimensions of $0.25 \times 0.15 \times 0.05$ mm was mounted on a Rigaku AFC-7R diffractometer with monochromatized Mo$K\alpha$ radiation. The crystal system is orthorhombic with cell parameters $a =$ 14.3298(6) Å, $b = 9.8906(6)$ Å, and $c = 8.3950(8)$ Å determined from 25 reflections of $37.77° < 2\theta < 39.90°$. A unit cell volume of 1189.8(1) Å^3 corresponds to $Z = 8$. The systematic extinction gave possible space groups *Ibam* and *Iba*2. Data collection was performed up to $2\theta = 80°$ using the ω–2θ scanning method ($\Delta\omega = 1.42 + 0.30 \tan\theta$) and no significant intensity decay (-0.8%) was detected from standard reflections monitored every 150 reflections. A total of 2072 reflections were collected, of which 1558 reflections with $I > 3\sigma(I)$ were used in the structure refinements. Empirical absorption corrections based on ψ scan were applied, resulting in transmission coefficients 0.580–1.000. All calculations of data processing and structural analysis were performed using the TEXSAN crystallographic software package (7).

The structure was determined by the following procedure. The space group *Ibam* was chosen since the statistical treatment of intensity data strongly preferred centrosymmety; a comparison with the space group *Iba*2 is discussed later. Three metal sites were located by the direct method, namely, one 16*k* and two 8*j* positions. Placing V atoms tentatively in the metal sites, we successfully located six oxygen sites in difference Fourier maps, namely, two 16*k* positions (O(1), O(6)), three 8*j* positions (O(2), O(3), O(4)), and one 8*f* position (O(5)). Oxygen coordinations of the metal sites were found to be octahedral (16*k*), tetragonal (8*j*), and trigonal bipyramidal (8*j*). The structure was successfully constructed by placing Co and V(1) atoms independently in the octahedral position with half-occupancies and V(2) and V(3) atoms in the tetragonal and trigonal-bipyramidal positions, respectively. The occupancies of Co and V(1) sites were checked to show the same value of 0.498(3) and thus fixed to 0.5. Co and V(1) atoms were refined isotropically because anisotropic U_{22} values for both atoms became almost zero or even negative presumably due to strong correlation between their positional and thermal parameters. V(2) and V(3) sites were confirmed to be fully occupied. O(5) atom initially placed in the 8*f* position exhibited large anisotropic displacements ($U_{11} = 0.015(1)$, $U_{22} = 0.031(2)$, $U_{33} = 0.019(1)$, $B_{eq} = 1.72(5)$ Å^2), suggesting an appropriate rearrangement of the O(5) position. The O(5) position was changed from 8*f* to 16*k* and from full occupancy to half-occupancy by introducing parameters of $y = \delta_1$ and $z = \frac{1}{4} - \delta_2$, which were refined to $\delta_1 = 0.011(1)$ and $\delta_2 = 0.013(2)$, and thereby the anisotropy was depressed ($U_{11} = 0.016(1)$, $U_{22} = 0.018(4)$, $U_{33} = 0.006(4)$, $B_{eq} = 1.1(1)$ Å^2). The structural basis of this rearrangement is described later. The revised model was refined to $R = 0.034$ and $R_w = 0.030$. The experimental and crystallographic data are listed in Table 1 and the atomic parameters and the isotropic temperature factors are in Table 2.

TABLE 2
Atomic Parameters, Isotropic Temperature Factors, and Occupancies for α-CoV_3O_8

Atom	Position	x	y	z	B_{eq} (Å^2)	Occupancy
Co	16*k*	0.1577(1)	0.8287(2)	0.3089(2)	0.58(3)	$\frac{1}{2}$
V(1)	16*k*	0.1521(1)	0.8363(2)	0.3112(3)	0.62(3)	$\frac{1}{2}$
V(2)	8*j*	0.29849(4)	0.94395(6)	0	0.504(8)	1
V(3)	8*j*	0.02252(4)	0.66658(6)	0	0.614(8)	1
O(1)	16*k*	0.0789(1)	0.7242(2)	0.1573(2)	1.37(4)	1
O(2)	8*j*	0.5824(2)	0.2761(3)	0	0.92(4)	1
O(3)	8*j*	0.7337(2)	0.4125(3)	0	0.90(4)	1
O(4)	8*j*	0.4200(2)	0.9826(3)	0	1.01(4)	1
O(5)	16*k*	0.1086(2)	0.011(1)	0.237(2)	1.1(1)	$\frac{1}{2}$
O(6)	16*k*	0.2678(1)	0.8531(2)	0.1638(2)	0.88(3)	1

RESULTS AND DISCUSSION

Description of α-CoV_3O_8 structure

Figure 1 depicts polyhedral representations of the α-CoV_3O_8 structure consisting of three polyhedral types: MO_6 (M = Co, V(1)) octahedra, V(2)O_4 tetrahedra, and V(3)O_5 trigonal bipyramids. Polyhedral units are presented in Fig. 2a for MO_6–MO_6 and Fig. 2b for V(2)O_4–V(3)O_5. Bond distances and angles for the polyhedra are listed in Table 3: as seen in Fig. 2a, two bond distances can be obtained for Co–O(5) (1.78(1), 2.02(1) Å) and V(1)–O(5) (1.69(1), 1.94(1) Å), from which the longer one of Co–O(5) and the shorter one of V(1)–O(5) are adopted from the considerations described in the next section. The polyhedral framework is constructed in the following manner. MO_6 octahedra are joined by sharing edges of O(2)–O(3) and O(6)–O(6) to form a zigzag chain running parallel to the c axis. The chains are connected by sharing O(5) vertices along the b axis to form an MO_6 octahedral slab standing in the bc plane as seen a corrugated wall in Figs. 1b and 3a. As depicted in Fig. 2b, a V(3)O_5 dimer is made by sharing an O(4)–O(4) edge to which two V(2)O_4 are attached by sharing O(4) vertices from opposite sides to form a V(2)O_4–V(3)O_5 unit. The MO_6 slabs are bridged by the V(2)O_4–V(3)O_5 units sharing O(3), O(6), and O(6) vertices of V(2)O_4 and O(1), O(1), and O(2) vertices of V(3)O_5. The framework structure exhibits an elongated hexagonal tunnel running parallel to the c axis as seen in Fig. 1*b*.

Valence States and Distribution of Co and V Atoms over the octahedral M site

Bond valence sums (BVS) (8) for metals and oxygens are listed in Table 4. The results indicate that both V(2) and V(3) are obviously pentavalent and that Co and V(1) are probably di- and tetravalent, respectively. As mentioned before, metal distribution over the M site can yield two values each for Co–O(5) and V(1)–O(5) distances that greatly affect the BVS values of Co, V(1), and O(5). The best BVS values for Co^{II}, $V(1)^{IV}$, and $O(5)^{II}$, listed in Table 4, were obtained from the bond distances given in Table 3. The metal distribution in the MO_6 slab to give the best BVS values is illustrated in Fig. 3: Fig. 3a shows how the MO_6 slab is built of MO_6 chains by sharing O(5) vertices and Fig. 3b shows the corresponding atomic arrangement. As shown in Fig. 3b and also in Fig. 2a, the Co and V(1) atoms occupy metal positions on opposite sides of the O(5) site and the O(5) atom occupies the site closer to the V(1) atom, resulting in the bond distances of Co–O(5) = 2.02 Å and V(1)–O(5) = 1.69 Å. However, the BVS values of 2.37 for Co^{II}, 3.66 for $V(1)^{IV}$, and 1.70 for $O(5)^{II}$ somewhat deviate from the ideal values. This is due to the difficulty in determining the exact positions of Co and V(1), which overlap each other. To sum up, as seen in Fig. 3b, the metal distribution over the M site is random in the MO_6 chain but constrained by a rule to give Co–O(5)–V(1) bonding between neighboring chains through the shared vertex O(5). This constraint results in the half-occupancies of Co and V(1) sites as well as the CoV_3O_8 formula.

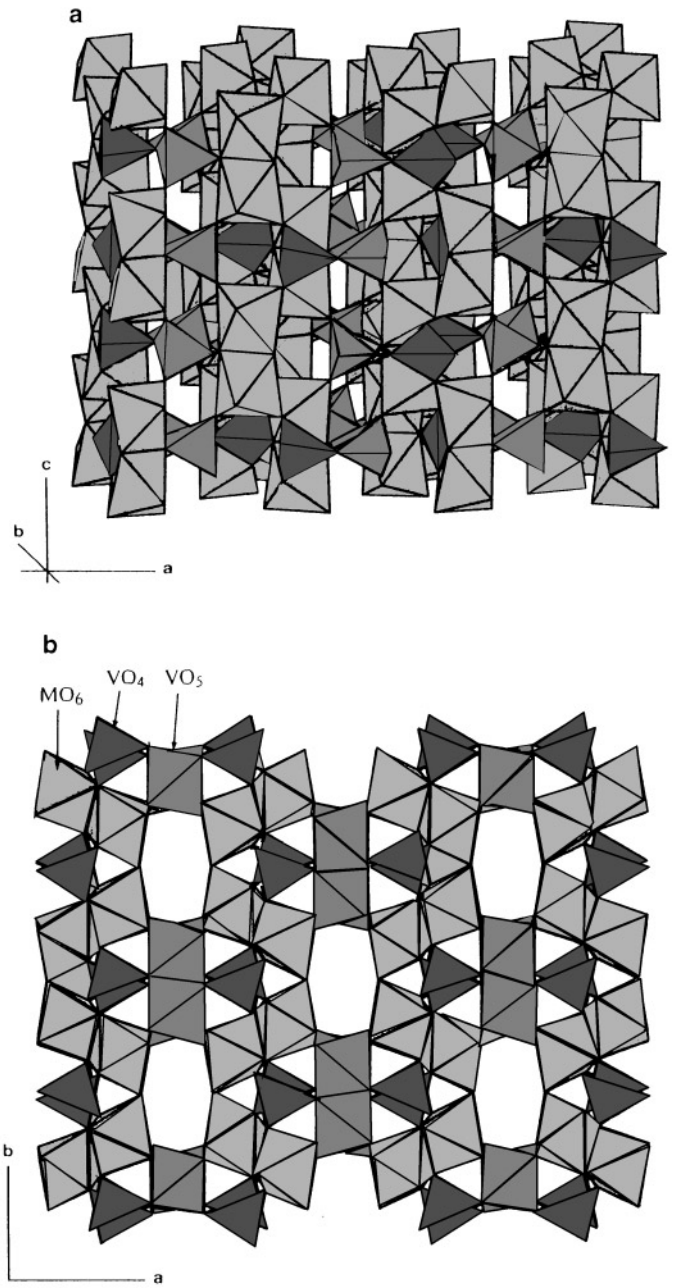

FIG. 1. Polyhedral representations of the crystal structure of α-CoV_3O_8: (a) perspective view; (b) projected view onto the *ab* plane.

Magnetic Susceptibility of α-CoV_3O_8

The magnetic susceptibility χ of α-CoV_3O_8 exhibits a sharp peak at 8.2 K in the χ–T curve that must be a Néel

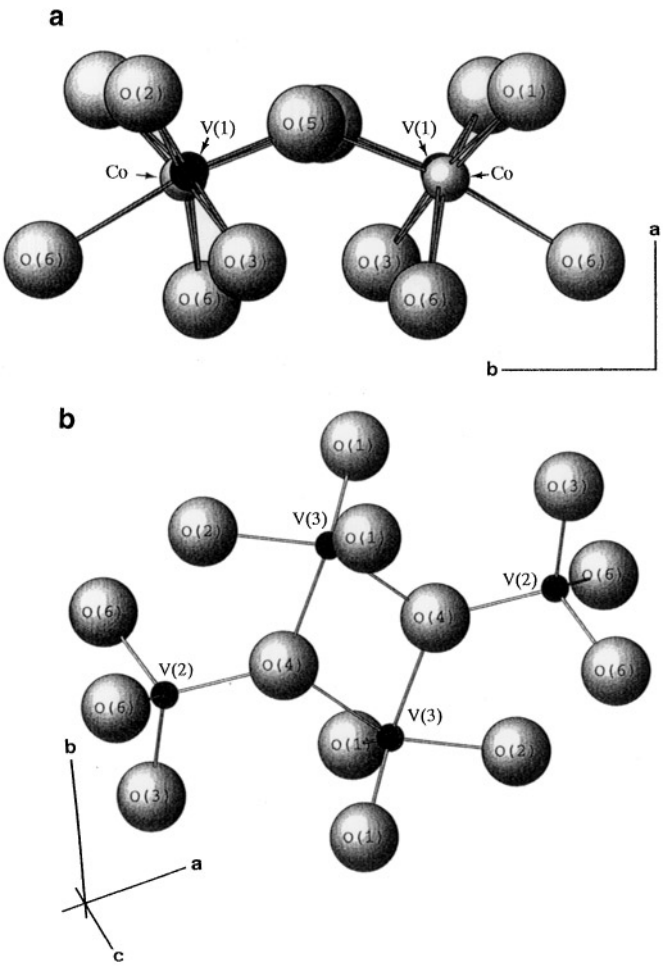

FIG. 2. Structures of polyhedral units: (a) MO_6–MO_6 (M = Co and V(1)) unit sharing O(5) vertex; (b) $V(2)O_4$–$V(3)O_5$ unit.

temperature below which antimagnetic order takes place. Typical Curie–Weiss paramagnetic behavior is observed above 9 K, yielding an effective moment of 5.75 μ_B and a Weiss constant of -32.1 K. The effective moment is in good agreement with the calculated value of 5.60 μ_B for one Co^{2+} ($S = 3/2$) and one V^{4+} ($S = 1/2$) ion in the formula CoV_3O_8. Since V(2) and V(3) are pentavalent, Co and V(1) are confirmed to be di- and tetravalent, respectively. The negative Weiss constant is indicative of antiferromagnetic interaction in the MO_6 slabs.

Comparison between Ibam and Iba2

There is another choice of space group for α-CoV_3O_8, namely, the noncentrosymmetric *Iba*2 as a replacement for the centrosymmetric *Ibam*. Actually, the structure of α-ZnV_3O_8 was determined using *Iba*2 instead of *Ibam* (4), but the reason for this choice was not described. To work out the space group problem, the α-CoV_3O_8 structure was modified using the space group *Iba*2 by placing all the atoms in 8*c* positions. The structure was refined to $R = 0.034$ and $R_w = 0.041$ for 110 variables, which are compared with $R = 0.034$ and $R_w = 0.030$ for 67 variables for the space group *Ibam*. The structural difference is seen in the atomic positions of the MO_6 slab as depicted in Fig. 4. For the space group *Ibam* (Fig. 4a), Co, V(1), and O(5) sites are half-occupied whereas for *Iba*2 (Fig. 4b) their sites are clearly separated and arranged in an ordered array. The bond distances for *Iba*2 become Co–O(5) = 1.97(1) Å and V(1)-O(5) = 1.75(1)Å, which give BVS values 2.55, 3.31, and 1.54 for Co, V(1), and O(5), respectively, being even worse

TABLE 3
Bond Distances (Å) and Angles (°) for Polyhedra in α-CoV_3O_8[a]

	CoO_6 octahedron		
Co–O(1)	1.991(3)	Co–O(2)^{i}	2.002(2)
Co–O(3)^{i}	2.109(3)	Co–O(5)^{ii}	2.02(1)
Co–O(6)	2.008(2)	Co–O(6)^{iii}	2.105(2)
O(1)–Co–O(2)^{i}	94.1(2)	O(1) –Co–O(3)^{i}	169.6(2)
O(1)–Co–O(5)^{ii}	94.3(4)	O(1) –Co–O(6)	96.8(2)
O(1)–Co–O(6)^{iii}	85.1(2)	O(2)^{i} –Co–O(3)^{i}	76.8(2)
O(2)^{i}–Co–O(5)^{ii}	111.3(3)	O(2)^{i}–Co–O(6)	160.3(1)
O(2)^{i}–Co–O(6)^{iii}	87.9(1)	O(3)^{i}–Co–O(5)^{ii}	93.2(4)
O(3)^{i}–Co–O(6)	89.4(2)	O(3)^{i}–Co–O(6)^{iii}	90.6(2)
O(5)^{ii}–Co–O(6)	89.2(3)	O(5)^{ii}–Co–O(6)^{iii}	165.8(3)
O(6)–Co–O(6)^{iii}	76.8(1)		
	$V(1)O_6$ octahedron		
V(1)–O(1)	2.000(3)	V(1)–O(2)^{i}	1.966(3)
V(1)–O(3)^{i}	2.109(3)	V(1)–O(5)^{ii}	1.69(1)
V(1)–O(6)	2.075(3)	V(1)–O(6)^{iii}	2.208(3)
O(1)–V(1)–O(2)^{i}	95.0(2)	O(1)–V(1)–O(3)^{i}	167.0(2)
O(1)–V(1)–O(5)^{ii}	98.5(4)	O(1) –V(1)–O(6)	94.4(2)
O(1) –V(1)–O(6)^{iii}	82.2(1)	O(2)^{i} –V(1)–O(3)^{i}	77.5(2)
O(2)^{i}–V(1)–O(5)^{ii}	106.1(4)	O(2)^{i} –V(1)–O(6)	155.7(2)
O(2)^{i}–V(1)–O(6)^{iii}	85.9(2)	O(3)^{i}–V(1)–O(5)^{ii}	93.7(4)
O(3)^{i}–V(1)–O(6)	88.8(2)	O(3)^{i}–V(1)–O(6)^{iii}	86.7(2)
O(5)^{ii}–V(1)–O(6)	94.6(4)	O(5)^{ii} –V(1)–O(6)^{iii}	167.8(4)
O(6)–V(1)–O(6)^{iii}	73.2(1)		
	$V(2)O_6$ tetrahedron		
V(2)–O(3)^{iv}	1.696(3)	V(2)–O(4)	1.783(2)
V(2)–O(6)	1.701(2)	V(2)–O(6)^{v}	1.701(2)
O(3)^{iv}–V(2)–O(4)^{v}	110.8(1)	O(3)^{iv} –V(2)–O(6)^{v}	107.44(7)
O(3)^{iv}–V(2)–O(6)^{vi}	107.44(7)	O(4)^{v}–V(2)–O(6)^{v}	111.50(7)
O(4)^{v}–V(2)–O(6)^{vi}	111.50(7)	O(6)^{v} –V(2)–O(6)^{vi}	108.0(1)
	$V(3)O_5$ trigonal bipyramid		
V(3)–O(1)	1.650(2)	V(3)–O(1)^{v}	1.650(2)
V(3)–O(2)^{vi}	1.854(3)	V(3)–O(4)^{iv}	2.082(3)
V(3)–O(4)^{vii}	1.997(3)		
O(1)–V(3)–O(1)^{v}	106.3(1)	O(1) –V(3)–O(2)^{vi}	101.26(8)
O(1)–V(3)–O(4)^{iv}	126.19(7)	O(1) –V(3)–O(4)^{vii}	96.48(8)
O(1)^{v}–V(3)–O(2)^{vi}	101.26(8)	O(1)^{v} –V(3)–O(4)^{iv}	126.18(7)
O(1)^{v}–V(3)–O(4)^{vii}	96.48(8)	O(2)^{vi}–V(3)–O(4)^{iv}	80.9(1)
O(2)^{vi}–V(3)–O(4)^{vii}	150.1(1)	O(4)^{iv} –V(3)–O(4)^{vii}	69.2(1)

[a]Symmetry codes: *i*, $x-1/2$, $y+1/2$, $z+1/2$; *ii*, x, $y+1$, z; *iii*, $1/2-x$, $3/2-y$, $1/2-z$; *iv*, $x-1/2$, $3/2-y$, z; *v*, $x,y, -z$; *vi*, $1/2-x$, x, $1/2+y$, z; *vii*, $1/2-x$, $y-1/2$, z.

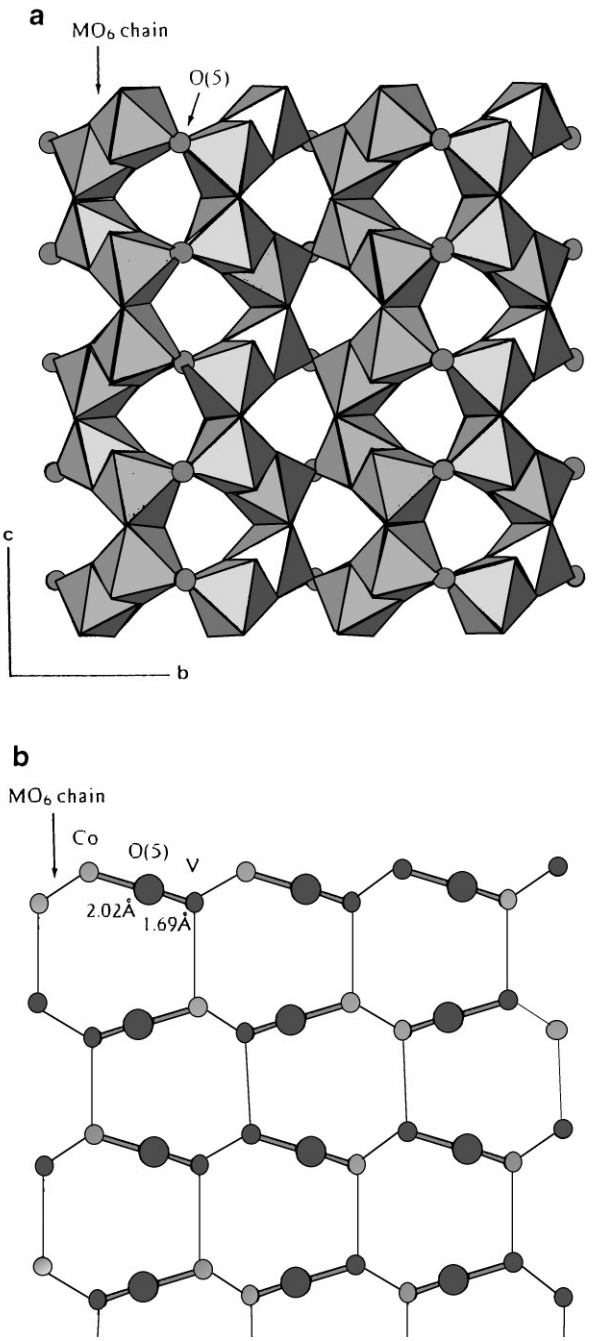

FIG. 3. MO_6 slab standing in the *bc* plane: (a) polyhedral representation showing linkages of MO_6 chains through O(5) atoms denoted by shaded circles; (b) an example of the atomic arrangement of Co, V(1), and O(5) atoms denoted by small open, small shaded, and large shaded circles, respectively.

than those for *Ibam*. Moreover, the site occupancies of Co and V(1), fixed to unity in the foregoing calculations, were refined to 0.93(1) and 1.07(2), respectively, both of which correspond to 25 e/atom, namely, the mean value of electron numbers of Co and V. This indicates that half of the Co site is occupied by a V atom and half of the V(1) site is occupied by a Co atom just as in the case of *Ibam*. Consequently, judging from the reliability factors, the BVS values, and the site occupancies, the space group *Iba*2 should be ruled out.

TABLE 4
Bond Valence Sums for Individual Atoms of α-CoV_3O_8

	Co	V(1)	V(2)	V(3)	Total
O(1)	0.45	0.56		1.51,1.51	2.02[a]
O(2)	0.43	0.61		0.87	1.91
O(3)	0.32	0.42	1.34		2.08
O(4)			1.06	0.47, 0.59	2.12
O(5)	0.41	1.29			1.70
O(6)	0.43, 0.33	0.46, 0.32	1.32, 1.32		2.08[b]
Total	2.37	3.66	5.04	4.96	

[a](0.45 + 0.56)/2 + 1.51.
[b](0.43 + 0.33)/2 + (0.46 + 0.32)/2 + 1.32.

Structural Relation between the α and β forms

It was reported that α-CoV_3O_8 transforms to β-CoV_3O_8 at 650°C, which crystallizes in the *C*-centered monoclinic system (2). Unfortunately, we failed to obtain single crystals of the β form by heating α-form crystals in an evacuated silica tube. The β phase also exists in A = Mg and Zn (2, 3), of which β-MgV_3O_8 has been structurally characterized by Saux and Galy (5): $C2/m$ with $a = 10.293(9)$ Å, $b = 8.530(8)$Å, $c = 7.744(8)$ Å, $\beta = 119.5(5)^\circ$, and $Z = 4$. It is quite likely that the structure of β-MgV_3O_8 is the same as that of β-CoV_3O_8 and then we can compare the α and β forms. The structure of the β form consists of MO_6 octahedra (M = Mg, V) and VO_4 tetrahedra. The octahedral M site is occupied equally by Mg and V atoms, which were refined using the same atomic parameters (5). Furthermore, MO_6 chains are linked by sharing vertices of O(1) to form an MO_6 slab which stands in $(10\bar{2})$ as shown in Fig. 5. The MO_6 slab of the β form is structurally similar to that of the α form (Fig. 3a) but is different in the locations of shared vertices. The MO_6 slabs of the β form are bridged through a V_2O_7 or VO_4–VO_4 unit made of two VO_4 tetrahedra by sharing vertices. This VO_4–VO_4 unit is compared to the $V(2)O_4$–$V(3)O_5$ unit in the α form. According to Saux and Galy (5), the M site of the β form is statistically occupied by Mg^{2+} and V^{4+} ions, but no further discussion was given. Judging from the structural analogy of the MO_6 slabs between the α and β forms, we believe that the Mg and V atoms are distributed so that the O(1) atom of the shared vertex bonds to the Mg and V atoms on opposite sides in the same manner as the Co and V atoms in the α form. If this is true, the O(1) atom in the 4*g* position (0, y, 0) must shift to the side of the V atom. This can be realized by converting

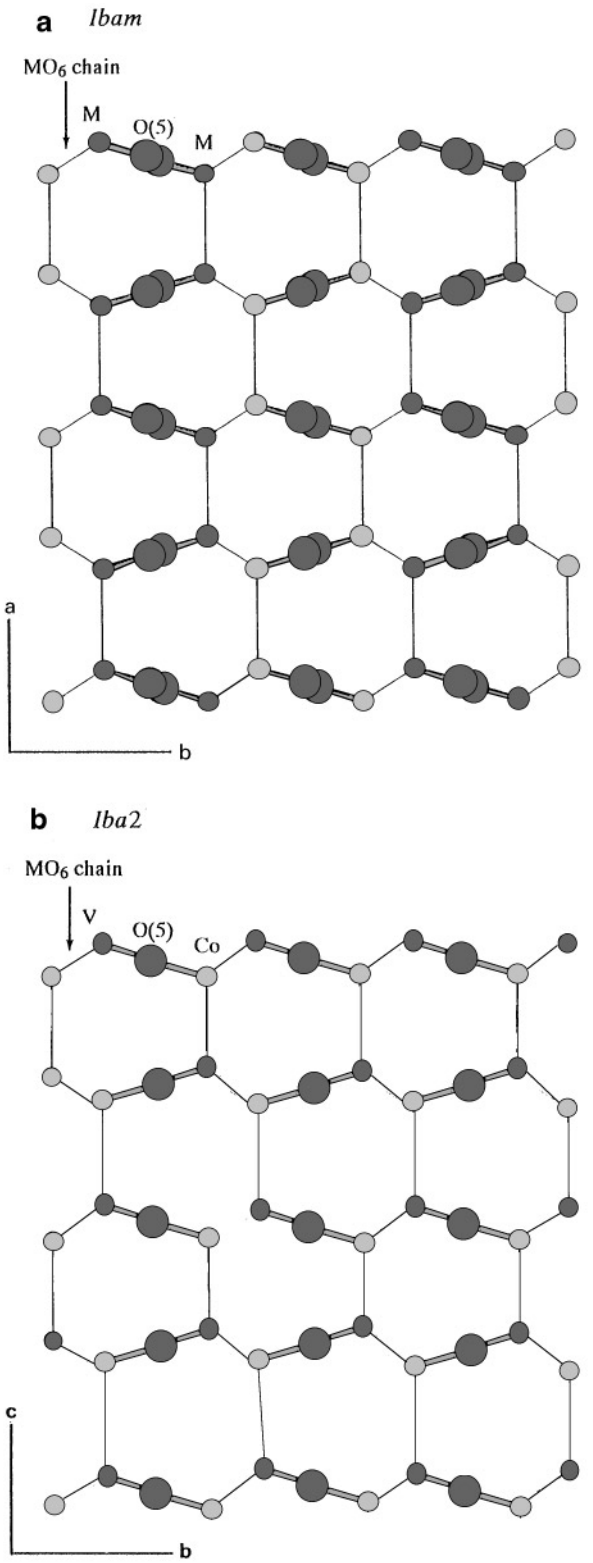

FIG. 4. Comparison of arrangement of atom sites in the MO_6 slabs between the space groups (a) *Ibam* and (b) *Iba*2. Atom sites of Co, V(1), and O(5) are denoted by small open, small shaded, and large shaded circles, respectively.

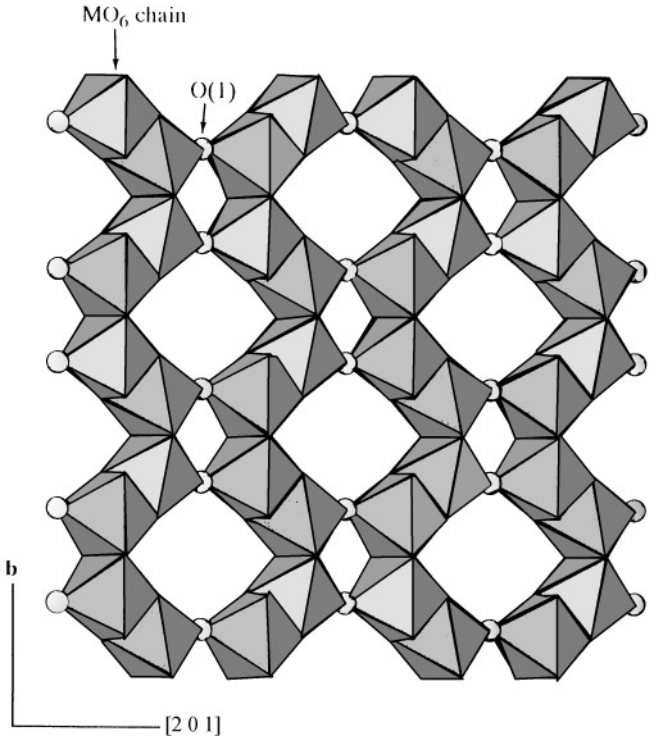

FIG. 5. MO_6 slab of β-form crystal standing in $(10\bar{2})$ for β-MgV_3O_8 (Ref. 5). Shaded circles denote O(1) atoms of shared vertices of neighboring MO_6 chains.

the 4*g* position to a half-occupied 8*j* position (x, y, z) with parameters of $x = -\delta_1$ and $z = -\delta_2$ just like the positional change of the O(5) atom of the α form from 8*f* $(x, 0, 1/4)$ to 16*k* $(x, \delta_1, \frac{1}{4} - \delta_2)$. In conclusion, the structures of the α and β forms are analogous, particularly in the construction of MO_6 slabs.

CONCLUSION

The structure of α-CoV_3O_8 has been determined based on the space group *Ibam*, which has been proved to be more appropriate than the space group *Iba*2. The structure consists of MO_6 (M = Co, V) octahedral slabs and VO_4–VO_5 units and the slabs are made of edge-sharing MO_6 zigzag chains. α-CoV_3O_8 is a typical class I mixed-valence ($V^{IV/V}$) compound (9), since V^{4+} ions occupy octahedral sites and V^{5+} ions occupy both tetraherdal and trigonal-bipyramidal sites. Related class I mixed-valence compounds are found in BaV_3O_8 (10) with $V^{IV}O_6$ octahedra and $V^{V}O_4$ tetrahedra and $A_2V_3O_8$ (A = K (11), Rb (12), NH_4 (13)) with $V^{IV}O_5$ square pyramids and $V^{V}O_4$ tetrahedra. A striking structural feature of α-CoV_3O_8 is seen in the metal distribution over the M site in which Co and V atoms equally reside. The metal distribution is basically random but is constrained by the rule that the two metals on opposite sides of the vertex

shared by neighboring MO_6 chains must be Co and V. This rule guarantees the equal occupations of Co and V, in other words the stoichiometric formula CoV_3O_8. The magnetic susceptibility data suggest some antiferromagnetic order in the MO_6 slabs.

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REFERENCES

1. P. Hagenmuller, *Prog. Solid State Chem.* **5,** 71 (1971).
2. A. Casalot and P. Hagenmuller, *J. Inorg. Nucl. Chem.* **31,** 3049 (1969).
3. J. Galy and M. Pouchard, *Bull. Soc. Chim. Fr.* 261 (1967).
4. D. J. Lloyed and J. Galy, *Cryst. Struct. Commun.* **2,** 209 (1973).
5. M. Saux and J. Galy, *C. R. Acad. Sci., Ser. C* **276,** 81 (1973).
6. Y. Oka, T. Yao, and N. Yamamoto, *J. Solid State Chem.* **86,** 116 (1190).
7. TEXSAN: Crystal Structure Analysis Package, Molecular Structure Corp., The Woodland, TX, 1985, 1992.
8. I. D. Brown and D. Altermatt, *Acta Crystallogr. Sect. B* **41**, 244 (1985).
9. M. B. Robin and P. Day, *in* "Advances in Inorganic Chemistry and Radiochemistry" (H. J. Emeléus and A. G. Sharpe, Eds.), Vol. 10, pp. 247–422. Academic Press, New York, London, 1967.
10. Y. Oka, T. Yao, and N. Yamamoto, *J. Solid State Chem.* **117**, 407 (1995).
11. J. Galy and A. Carpy, *Acta Crystallogr., Sect. B* **31**, 1794 (1975).
12. M.-L. Ha-Eierdanz and U. Z. Müller, *Z. Anorg. Allg. Chem.* **613,** 63 (1992); G. Liu and J. E. Greedan, *J. Solid State Chem.* **144**, 499 (1995).
13. F. R. Théobald, J.-G. Théobald, J. C. Verdrine, R. Clad, and J. Renard, *J. Phys. Chem. Solids* **45,** 581 (1984).