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Crystal Structures and Transition Mechanism of $VO_2(A)$

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Structures of $VO_2(A)$ have been redetermined by single-crystal diffractometry for low- (LTP) and high-temperature (HTP) phases at 298 and 473 K, respectively. The LTP adopts the tetragonal system $P4/ncc$ with $a = 8.4403(9)$ Å, $c = 7.666(1)$ Å, and $Z = 16$, whereas the HTP adopts the body-centered tetragonal system $I4/m$ with $a = 8.476(2)$ Å, $c = 3.824(2)$ Å, and $Z = 8$. The refinements led to $R/R_w = 0.031/0.032$ for LTP and 0.012/0.033 for HTP. The structures of both phases consist of edge-sharing VO_6 octahedra and exhibit quite similar oxygen frameworks. Through the transition the V^{4+}–V^{4+} bonding in LTP with a distance of 2.7695(8) Å is dissociated in HTP to a distance of 3.0794(3) Å. The transition occurs with cooperative movements of the V atoms, namely, a rotation around the c axis and a shift along the c axis. Strangely, twinning is induced on the LTP to HTP transition but disappears on the reverse transition. © 1998 Academic Press

INTRODUCTION

There are several VO_2 polymorphs among which $VO_2(A)$ is a metastable phase synthesized exclusively by hydrothermal methods (1). We have made several studies to elucidate the structures and properties of $VO_2(A)$ and found a phase transition due to V^{4+}–V^{4+} bonding occurring around 162°C on heating similar to that in the rutile-type VO_2 (2–4). The structure of $VO_2(A)$ for the low-temperature phase (LTP) was first determined from powder X-ray diffraction data by the Rietveld method: the tetragonal system $P4_2/nmc$ with $a = 8.4336(7)$ Å, $c = 7.6782(7)$ Å, and $Z = 16$ (3) was used. The high-temperature phase (HTP) was studied by the same method to clarify the transition mechanism; however, neither the true unit cell nor the appropriate space group could be determined (4). We are now successful in growing single crystals of $VO_2(A)$ and determining crystal structures for both phases. In the present paper, we report the structural details and the transition mechanism.

EXPERIMENTAL

Single crystals of $VO_2(A)$ were obtained by the hydrothermal treatment of a $VOCl_2$–$FeCl_2$ mixed solution sealed in a silica ampoule at 330°C for 30 h. Brownish black crystals with a platelike shape were confirmed to be $VO_2(A)$ by Weissenberg camera work and also to be free from iron by EDX analysis. A crystal with dimensions of 0.20 × 0.20 × 0.15 mm was mounted on a Rigaku AFC-7R diffractometer and data collections were made at 298 K for LTP and at 473 K for HTP. Experimental details and crystallographic data are listed in Table 1. Possible space groups were $P4/ncc$ for LTP and $I4$, $I\bar{4}$, or $I4/m$ for HTP. Structures of both phases were solved by the Patterson method. The LTP structure was straightforwardly refined to $R = 0.031$, $R_w = 0.032$, and $S = 1.32$, whereas the refinement of the HTP structure was extremely difficult. Trial refinements of plausible order–disorder models never converged to R values less than 0.2. Finally, the HTP crystal was thought to be twinned; namely, the c axes of neighboring twin individuals take inverse directions to each other. Structures for the three space groups were separately refined on the assumption of the twinning. The $I\bar{4}$ structure did not converged. The $I4$ and $I4/m$ structures were successfully refined to nearly equal R values. The z coordinates of all atoms in the $I4$ structure were very close to each other, suggesting a (001) mirror plane. Therefore, the space group $I4/m$ was adopted and the structure was finally refined to $R = 0.012$, $R_w = 0.033$, and $S = 1.20$ at a twin ratio of 0.395/0.605(1). The untwinned uniform LTP crystal was recovered on cooling as confirmed by the remeasured diffraction data at 298 K. All the data processing and structure refinement calculations were performed with the TEXSAN software package (5) and SHELXL-93 (6) partly for HTP. The atomic coordinates and temperature factors are given in Table 2.

RESULTS AND DISCUSSION

Structures of LTP and HTP

Figure 1 depicts the structures of $VO_2(A)$ for LTP and HTP; Table 3 lists bond lengths in the VO_6 octahedron and

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TABLE 1
Experimental and Crystallographic Parameters for $VO_2(A)$

Phase	LTP	HTP
Temperature (K)	298	473
Space group	$P4/ncc$	$I4/m$
a (Å)	8.4403(9)	8.476(2)
c (Å)	7.666(1)	3.824(2)
V (Å^3)	546.1(1)	274.7(2)
Z	16	8
D_c (g cm^{-3})	4.035	4.010
λ (Mo$K\alpha$) (Å)	0.71069	0.71069
μ (cm^{-1})	66.3	65.9
$2\theta_{\max}$ (deg)	80	80
Scan technique	2θ–ω	2θ–ω
Scan width, $\Delta\omega$ (deg)	$1.63 + 0.30 \tan\theta$	$1.63 + 0.30 \tan\theta$
Absorption correction	ψ scan	ψ scan
Transmission factors	0.606–0.630	0.613–0.623
Number of unique reflection ($I > 0$)	838	476
Number of reflection ($I > n\sigma(I)$)	511 ($n = 3$)	453 ($n = 2$)
Number of variables	30	21
Minimization function	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\sum w(\lvert F_o\rvert^2 - \lvert F_c\rvert^2)^2$
R	0.031	0.012
R_w	0.032	0.033 (all data)
w	$[\sigma^2(F_o^2) + (0.0250P)^2]^{-1}$ $P = (F_o^2 + 2F_c^2)/3$	$[\sigma^2(F_o^2) + (0.0228P)^2]^{-1}$ $P = (F_o^2 + 2F_c^2)/3$
S	1.32	1.20
$\Delta\rho_{\max/\min}$ (e/Å^3)	0.92/ − 1.32	0.34/ − 0.61

TABLE 3
Interatomic Distances (Å) in $VO_2(A)$[a]

	LTP	HTP
	VO_6 octahedra	
V–O(1)	1.949(5)	1.9652(2)
V–O(1)^{i}	1.980(5)	1.9652(2)
V–O(1)^{ii}	1.981(2)	2.005(1)
V–O(1)^{iii}	2.269(2)	2.272(1)
V–O(2)^{ii}	1.645(2)	1.648(1)
V–O(4)^{iv}	1.976(2)	1.971(1)
	V–V distances	
V–V^{ii}	2.7695(8)	3.0794(3)
V–V^{v}	3.1022(7)	3.0794(3)
V–V^{vi}	3.2472(8)	3.0794(3)
V–V^{vii}	3.3729(9)	3.4139(7)

[a] Symmetry codes: ^{i} $x,3/2 - y,z - 1/2$; ^{ii} $1 - y,1 - x,1/2 - z$; ^{iii} $y - 1/2, x + 1/2,1/2 - z$; ^{iv} $1 - x,y + 1/2,1/2 - z$; ^{v} $y - 1/2, - x, - z$; ^{vi} $y - 1/2, x + 1/2,1/2 - z$; ^{vii} $1/2 - x,1/2 - y, - z$. Symmetry codes are given for LTP.

V–V distances. The LTP structure is similar to that of the previous study (3); the space group $P4/ncc$ instead of $P4_2/mnc$ is verified. The HTP structure exhibits the space group $I4/m$ with $a_H \approx a_L$ and $c_H \approx \frac{1}{2}c_L$, where ($a_L$, c_L) and (a_H, c_H) denote lattice parameter sets of LTP and HTP, respectively. Both structures consist of VO_6 octahedra where V atoms are placed in off-center positions nearer to O(2), thus showing one short V–O distance such as V–O(2) = 1.645(2) Å for LTP and 1.648(1) Å for HTP. The oxygen frameworks of LTP and HTP are virtually identical as shown in Fig. 1a. The essential structural difference is thus seen in the arrangements of V atoms. In LTP (Fig. 1b), the V atoms form slight-zigzag lines running in the c direction with a c_L period; the y coordinates take alternate signs in turn due to the c glide plane. In HTP (Fig. 1c) the V atoms are rearranged to form straight lines with a $1/2 \times c_L$ period; the y coordinates take selectively either positive or negative sign. As the oxygen framework has a nearly $1/2 \times c_L$ period in LTP, the rearrangement of V atoms from LTP to HTP results in the reduced cell $c_H \approx c_L/2$ together with twin formation as described later.

TABLE 2
Atomic Coordinates and Isotropic Temperature Factors for $VO_2(A)$

Atom	x	y	z	B_{eq} (Å^2)
		LTP, space group $P4/ncc$		
V	0.44818(5)	0.72455(5)	0.12939(5)	0.418(6)
O(1)	0.4039(2)	0.7481(2)	0.3776(6)	0.59(2)
O(2)	0.4099(2)	0.4108(2)	0.3732(7)	0.78(3)
		HTP, space group $I4/m$		
V	0.30024(2)	0.02543(2)	0	0.585(4)
O(1)	0.4995(1)	0.1528(1)	0	0.69(1)
O(2)	0.1601(1)	0.1601(1)	0	1.04(1)

Transition Mechanism between LTP and HTP

Since the exact structures of LTP and HTP have been determined, the transition mechanism is now disclosed. We consider the transition mechanism utilizing the movements of the V–V pair as defined by a V-atom pair in the ab plane connected with a thick solid line as shown in Fig. 2a (V–V = 3.3729 Å for LTP, V–V = 3.4139 Å for HTP). The principal feature of the transition is formation and dissociation of V^{4+}–V^{4+} bonding (3, 4). That is, the V atoms are located with an even V–V distance of 3.0794 Å along the c axis in HTP (Fig. 2b, right), which changes in LTP (Fig. 2b, left) to alternate distances of 2.7695 and 3.1022 Å, of which the former obviously manifests the V^{4+}–V^{4+} bonding. In both LTP and HTP, the V–V pairs are not parallel to ⟨100⟩ but inclined by 7.2° (Fig. 2a). In LTP, the V–V pairs are placed along the c axis at $z = 0.0044, 0.2456, 0.5044$, and 0.7456 in terms of c_L; note that the origin of c_L is moved to the origin of c_H, namely, to $z = 0.125$ of the original lattice. In HTP, V–V pairs are placed at $z = 0$ and $z = 0.5$ in terms of c_H. On the transition from LTP to HTP, as indicated by

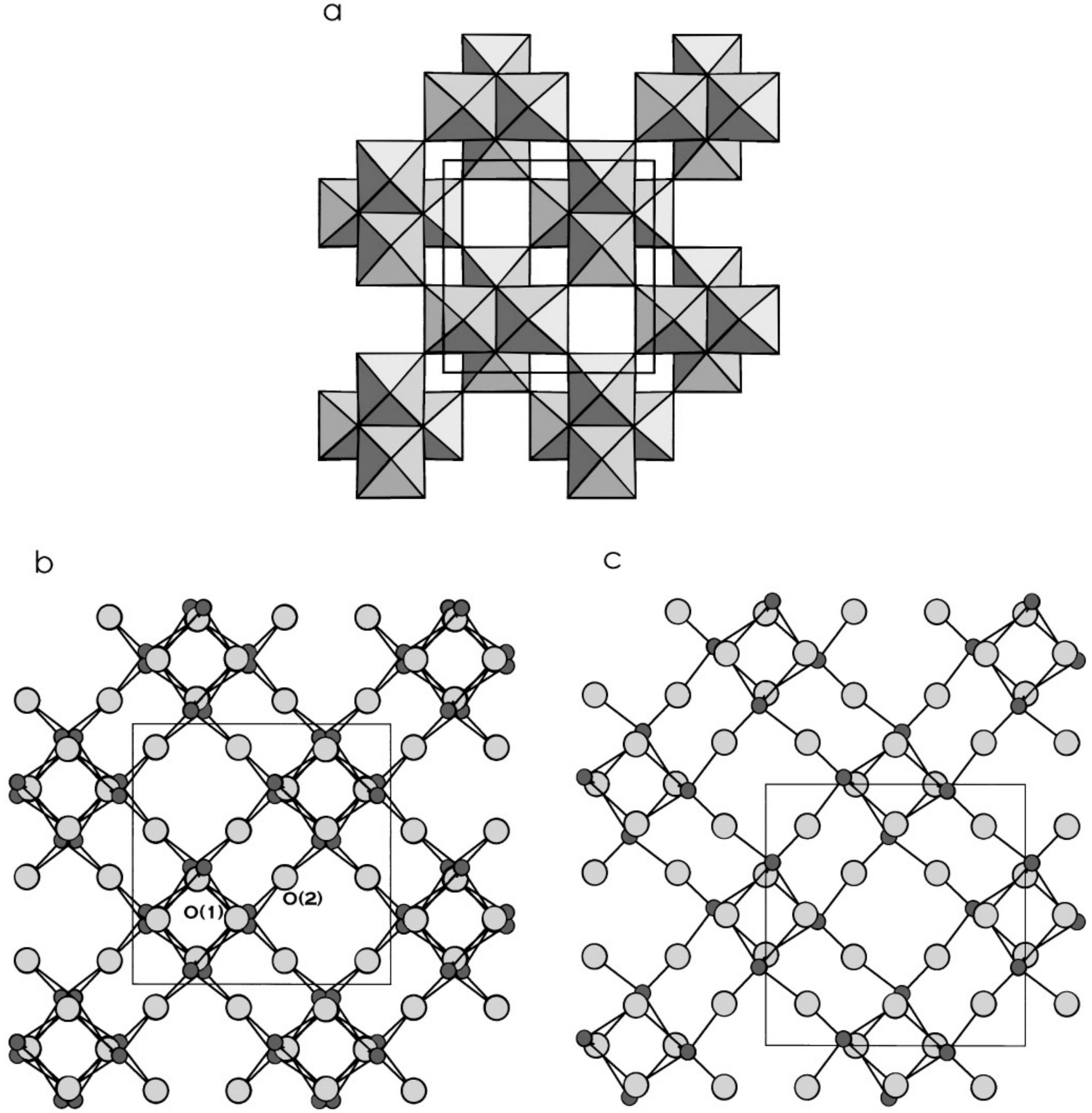

FIG. 1. Structures of $VO_2(A)$ projected along the *c* axis: (a) VO_6 octahedral framework or oxygen framework in common between LTP and HTP; (b) LTP structure; (c) HTP structure. In (a), a unit cell of LTP is indicated by solid lines. In (b) and (c), V and O atoms are denoted by small and large circles, respectively, and unit cells are indicated by thin solid lines.

arrows in Fig. 2b, right, V–V pairs at $z = 0.2456$ and $z = 0.5044$ rotate around the *c* axis by 14.5° and simultaneously shift along the *c* axis by 0.034 Å to $z = 0.25$ and $z = 0.50$, respectively; other V–V pairs at $z = 0.0044$ and $z = 0.7456$ just shift to $z = 0$ and $z = 0.75$, respectively. In this manner, V^{4+}–V^{4+} bonding (2.7695 Å) and nonbonding (3.1022 Å) in LTP are changed to have an even distance 3.0794 Å of a nonbonding V^{4+}–V^{4+} separation (7). As a result, the c_H axis becomes half of c_L ($c_H \approx 1/2 \times c_L$) and the primitive lattice is changed to the body-centered lattice. The transition from HTP to LTP proceeds reversely as indicated by arrows in Fig. 2b, right.

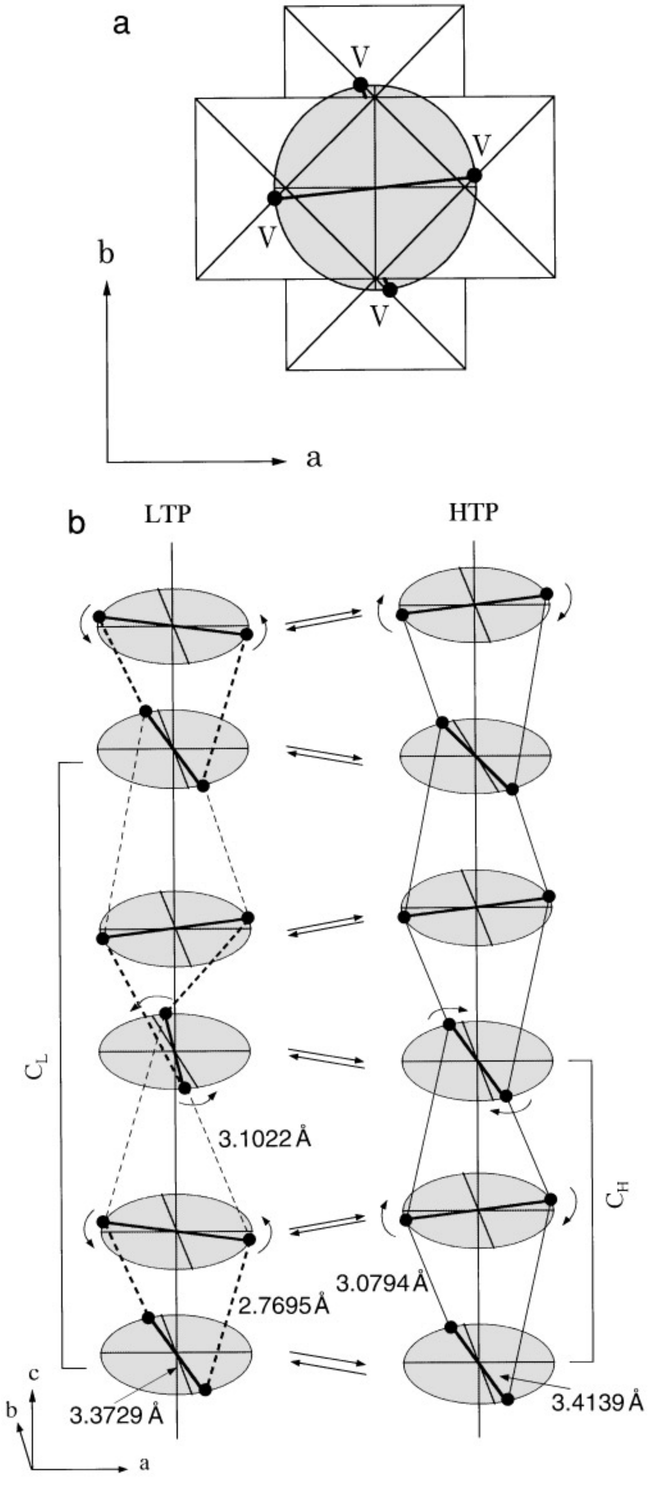

FIG. 2. Schematic diagrams to demonstrate the transition mechanism of $VO_2(A)$: (a) definition of V–V pair as two V atoms in edge-sharing VO_6 octahedra connected by a thick solid line in the *ab* plane; (b) phase transition between LTP (left) and HTP (right) represented by using V–V pairs stacked along the *c* axis. In (b), directions of atomic movements through the transitions are indicated by arrows and V^{4+}–V^{4+} bonding and nonbonding in LTP are indicated by thick and thin broken lines, respectively. See text.

Twin Formation in HTP and Recovery in LTP

It is unexpected that twinning appears on heating to HTP and disappears on cooling to LTP. The twinning is characterized by $\langle 100 \rangle$ or $\langle 110 \rangle$ twin axes of 180° rotation and, because of the centrosymmetric structure, by $\{100\}$ twin planes. The twinning is shown schematically in Fig. 3 using V–V pairs defined in Fig. 2a, where the twin interface is the (001) plane and the twin operation is 180° rotation around the [010] axis. It is noted that by this operation the oxygen framework exhibits no change. Across the interface a V–V pair rotates by 14.5° around the *c* axis (or changes signs of *x* or *y* coordinates of the V atoms) from its position of the untwinned structure. Since all the twin interfaces are parallel planes, the present twin is regarded as a polysynthetic twin which in this case makes the crystal look like a *single* crystal. Comparing Fig. 3 with Fig. 2b, left, we see that this positional relation between V–V pairs across the interface just corresponds to that between V–V pairs for V^{4+}–V^{4+} bonding in LTP. Consequently, it is presumed that on the transition from LTP to HTP the twin interfaces are introduced between the adjacent V–V pairs, forming V^{4+}–V^{4+}

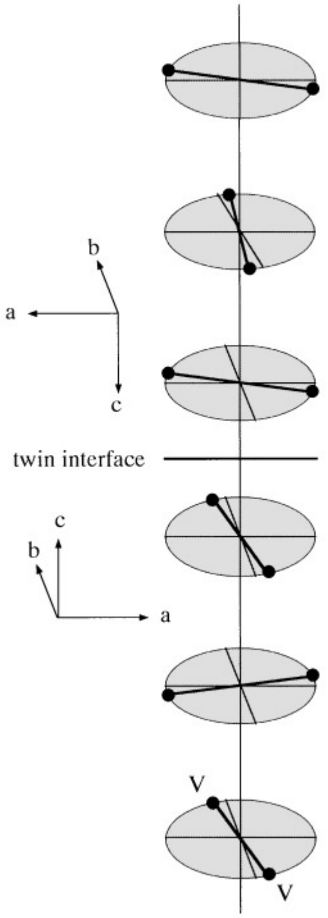

FIG. 3. Schematic diagram of crystallographic relation across the twin interface in HTP using a V–V pair stacking model along the *c* axis. See text.

bonding when the rotational movements, indicated by the arrows in Fig. 2b, left, fail to occur. However, on the transition from HTP to LTP the V–V pairs across the interfaces smoothly return to the positions for V^{4+}–V^{4+} bonding without making the rotational movements indicated by the arrows in Fig. 2b, right. In this manner it can occur that the unusual phenomenon that twinning in HTP vanishes in LTP.

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