BRIEF COMMUNICATION

A Structural Study of the High-Temperature Phase of VO$_2$(A)

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The high-temperature phase of VO$_2$(A) appearing above 435 K has been studied using the X-ray diffraction data at 200°C by the Rietveld method. The structure was analyzed based on the low-temperature phase with the tetragonal system ($P4_2/ncm$). It was detected that the cooperative rotation of V atoms around the c axis taking place during the phase transition results in the elongation of the shortest V–V distance of the low-temperature phase. The ^{51}V NMR study has clarified that the shortest V–V pairs in the low-temperature phase form nonmagnetic V^{4+}–V^{4+} pairs. The phase transition of VO$_2$(A) is concluded to originate in the dissociation of the V^{4+} ion pairs. © 1994 Academic Press, Inc.

INTRODUCTION

VO$_2$(A) is a polymorph of vanadium dioxide, as are the rutile-type VO$_2$ and VO$_2$(B). In the latter two polymorphs, V^{4+} ion pair formation and phase transitions due to dissociation of the ion pairs have been reported (1, 2). VO$_2$(A) exhibits a phase transition at 435 K and the behavior appears more similar to that of the rutile-type VO$_2$ (3). The low-temperature phase of VO$_2$(A) crystallizes in the tetragonal system $P4_2/ncm$ with $a = 0.84336$ nm and $c = 0.76782$ nm and from a structural point of view VO$_2$(A) has relationship with VO$_2$(B) (4). In the previous papers (3, 4), the nature of the phase transition of VO$_2$(A) was speculated to be the dissociation of V^{4+} ion pairs, in analogy with the phase transition of the rutile-type VO$_2$. However, the presence of V^{4+} ion pairs and the structure of the

high-temperature phase remained uncertain. The present work aims to elucidate the nature of the phase transition by structural analysis of the high-temperature phase and also by ^{51}V NMR study of the low-temperature phase.

EXPERIMENTAL

Powder samples of VO$_2$(A) were synthesized hydrothermally from VO(OH)$_2$ powders at 250°C; the details have been described elsewhere (4). Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku RAD-B system with Mo$K\alpha$ radiation at room temperature and 200°C. The measurement at 200°C was performed by blowing hot air onto the sample mounted on a glass sample holder. The XRD measurements were made by a step scanning method with a 2θ range of 5° to 50°, a step width of 0.01°, and a step time of 10 sec for room temperature and 4 sec for 200°C. The procedure of the Rietveld method was the same as that employed in the previous study (4). The ^{51}V NMR measurement was conducted at 77 K using a standard phase-coherent pulsed-type spectrometer at a fixed frequency of 16.3400 MHz.

RESULTS AND DISCUSSION

Figure 1 compares the XRD patterns for the low-temperature phase (LTP) at room temperature and the high-temperature phase (HTP) at 200°C. The difference in the two patterns is that some reflections, for example, 211 and 311 as denoted in Fig. 1, almost disappear in the HTP; however, the traces of the two peaks are still present at
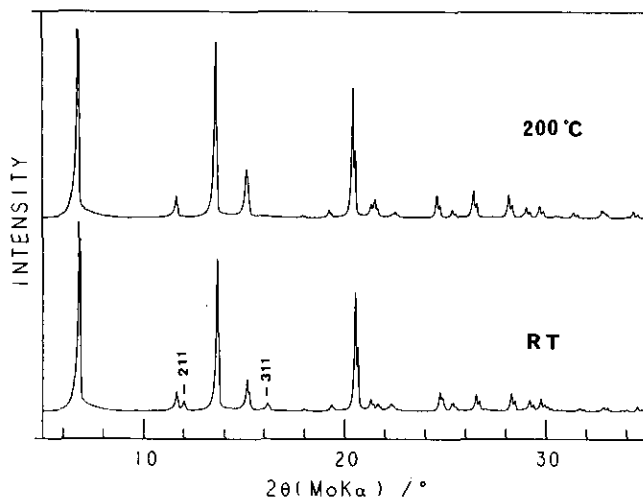
FIG. 1. Powder X-ray diffraction patterns of $VO_2(A)$ for the HTP at 200°C (top) and the LTP at room temperature (bottom).

200°C. It is suggested that the two patterns are essentially the same and therefore the structure of the LTP was adopted as a structural model of the HTP for the Rietveld analysis. The structure refinement based on the model led to the fit with the reliability factor $R_{wp} = 0.136$. The fit is presented in Fig. 2 and the crystallographic data are listed in Table 1. The VO_6 octahedral framework and the
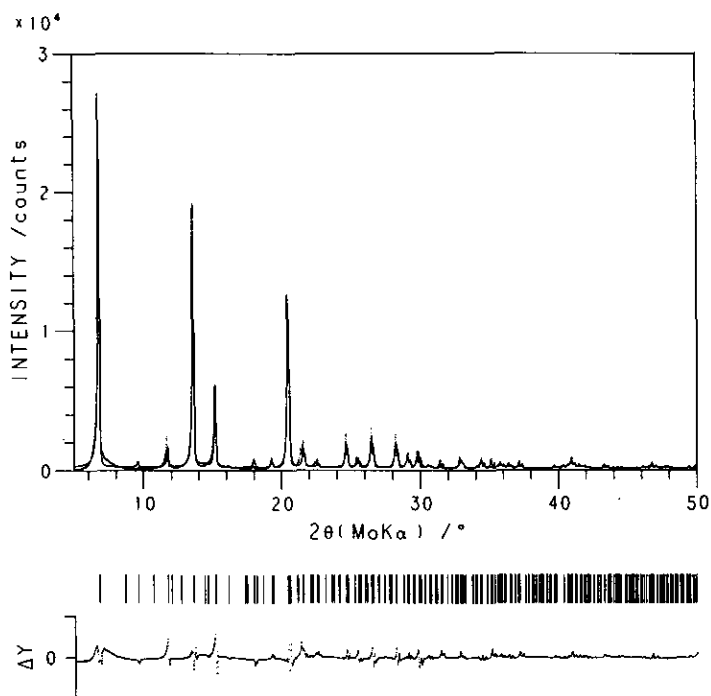

FIG. 2. Rietvelt refinement plot of $VO_2(A)$ for the HTP at 200°C. The calculated (solid line) and observed data (dots) are shown at the top with the positions of Bragg reflections (the vertical marks) in the middle and the difference trace at the bottom.

TABLE 1
Crystallographic Data for HTP of $VO_2(A)$ at 200°C

Atom	Position	x	y	z
V	16j	0.19195(5)	0.0050(2)	0.1161(3)
O(1)	16j	0.1600(1)	0.0107(5)	0.373(1)
O(2)	8i	0.1587(5)	0.1587(5)	0.351(2)
O(3)	8i	0.1404(5)	0.1404(5)	0.900(2)

Note. $P4_2/ncm$, $Z = 16$, $a = 0.84830(6)$ nm, $c = 0.76152(5)$ nm.

V atom positions are depicted in Fig. 3, together with those of the LTP for comparison. The V–V distances along the c axis for the V atoms specified in Fig. 3 are compared for both phases in Table 2. As indicated by the arrows in Fig. 3, V atoms cooperatively rotate around the c axis in the model to increase the V1–V4 (or V2–V3) distance and to decrease the V1–V3 (or V2–V4) distance, as can be seen from Table 2. It is noted that V1–V4 (or V2–V3) has the shortest V–V distance in the LTP, whereas the formation of V^{4+}–V^{4+} pairs was suggested in the previous study (4). The presence of the V^{4+} ion pairs in the LTP has been examined by the ^{51}V NMR measurements. As shown in Fig. 4, a ^{51}V NMR signal with a positive Knight shift of +0.18% was observed for the LTP. This result is interpreted similarly to the case of $VO_2(B)$ (2) as that the signal comes from nonmagnetic V^{4+} ions due to spin-singlet V^{4+}–V^{4+} pairs. Consequently, taking into account the structure and V–V distances of
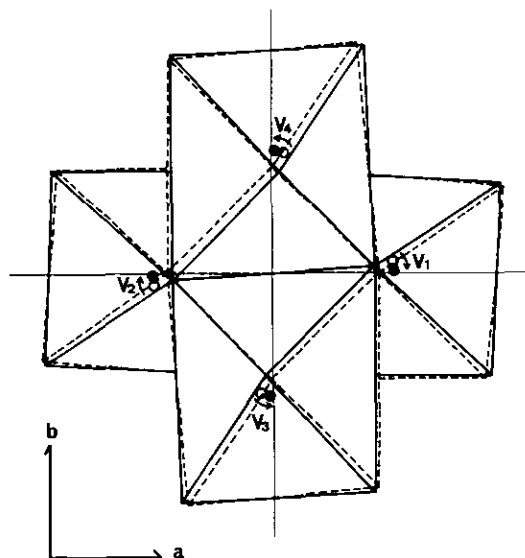

FIG. 3. VO_6 octahedral frameworks of $VO_2(A)$ viewed along the c axis for the HTP (solid line) and for the LTP (broken line) from (4). V atoms are represented by closed and open circles for the HTP and the LTP, respectively, and the arrows indicate the directions of atomic shifts on the transition from the LTP to the HTP.

TABLE 2

V–V Distances (nm) for LTP and
HTP of $VO_2(A)$

	LTP[a]	HTP
V1–V4[b]	0.2883(2)	0.3032(7)
V1–V3[b]	0.3196(2)	0.3121(7)

[a] Data from (4).
[b] The positions of V1, V3, and V4 are shown in Fig. 3.

FIG. 4. ^{51}V NMR spectrum of $VO_2(A)$ for the LTP operated at a constant frequency of 16.3400 MHz and taken at 77 K.

the LTP, the pairing evidently occurs along the c axis between V1 and V4 (or V2 and V3).

The revealed structure of the HTP displays the rotational shifts of V atoms around the c axis taking place during the phase transition. The shifts result in the elongation of the V–V pairs along the c axis which has the shortest distance in the LTP. The existence of nonmagnetic V^{4+}–V^{4+} pairs in the LTP has been confirmed by the ^{51}V NMR study and the shortest V–V pairs along the c axis are assigned to the nonmagnetic pairs. The previous study reported an increase in magnetic susceptibility during the transition from the LTP to the HTP (3). This indicates the development of magnetic V^{4+} ions by the dissociation of the nonmagnetic pairs. To sum up, the phase transition of $VO_2(A)$ is originated in the dissociation of the V^{4+}–V^{4+} pairs along the c axis. The nature of the phase transition of $VO_2(A)$ is thus analogous to those of the other polymorphs of rutile-type VO_2 and $VO_2(B)$.
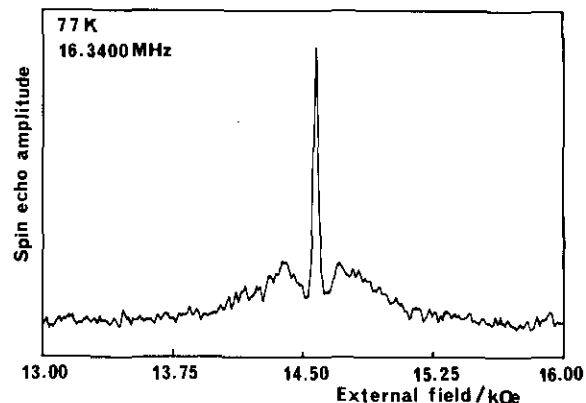
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