

The Incorporation of Vanadium in β -Rhombohedral Boron as Determined by Single-Crystal Diffractometry*

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The solubility of vanadium in β -rhombohedral boron has been studied by single crystal diffractometry for two crystals of composition $\text{VB}_{\sim 65}$ and $\text{VB}_{\sim 165}$. The space group is $R\bar{3}m$ and the hexagonal cell dimensions are $a = 10.972 \text{ \AA}$, $c = 23.908 \text{ \AA}$ for $\text{VB}_{\sim 65}$ and $a = 10.949 \text{ \AA}$, $c = 23.840 \text{ \AA}$ for $\text{VB}_{\sim 165}$. At the higher concentration of vanadium, the same two sets of holes are occupied as in $\text{CrB}_{\sim 41}$ and $\text{FeB}_{\sim 49}$. The boron framework is essentially the same as in undoped β -rhombohedral boron. Vanadium is found to expand the unit cell slightly. © 1986 Academic Press, Inc.

Introduction

Solid solutions of 3d transition elements in β -rhombohedral boron have been reported previously (1) and structure studies have been made for many of them (2, 3). We have been investigating properties of solutions of vanadium in β -boron and have grown single crystals containing 1.6 and 0.6 at.% vanadium. Since no detailed structure study of vanadium in β -boron has been reported we have made such a study for two single crystals with the compositions $\text{VB}_{\sim 65}$ and $\text{VB}_{\sim 165}$.

Experimental

The single-crystal pieces of vanadium-doped β -boron were harvested from polycrystalline boules produced from vanadium-boron melts held in chemically

vapor-deposited BN crucibles. For these melts 99.99% pure β -boron (4) zone-refined lumps, and 99.95% pure vanadium (5) rod were used. These were melted together in an rf-induction-heated crystal-growing furnace (6) employing a graphite susceptor and a blanketing atmosphere of pure argon at a pressure of 75 atm. These melts were slowly cooled at $\sim 2.2^\circ\text{C}/\text{min}$ and rapidly cooled at $\sim 350^\circ\text{C}/\text{min}$ from the melting temperature in order to grow the polycrystalline boules. The $\text{VB}_{\sim 65}$ sample was slowly cooled; the $\text{VB}_{\sim 165}$ sample was rapidly cooled. The boules contained single-crystal regions of the order of 2 to 4 mm in diameter. Some crystals of undoped β -boron were also grown by the rapid-cooling method.

Two small crystals were selected for the structure study. The dimensions of the $\text{VB}_{\sim 65}$ crystal were $0.3 \times 0.3 \times 0.1 \text{ mm}$ and for $\text{VB}_{\sim 165}$ they were $0.3 \times 0.1 \times 0.05 \text{ mm}$. Both crystals appeared to be of high quality on the basis of rotation photographs with X-rays.

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All X-ray measurements were made with an automated Nicolet P3F four-circle diffractometer (7) using graphite-monochromatized $\text{MoK}\alpha$ radiation (0.71069 Å). The space group was $R\bar{3}m$ with hexagonal cell dimensions of $a = 10.972(3)$ Å, $c = 23.908(9)$ Å for $\text{VB}_{\sim 65}$ and $a = 10.949(3)$ Å, $c = 23.840(10)$ Å for $\text{VB}_{\sim 165}$, and $a = 10.955(3)$ Å, $c = 23.855(6)$ Å for undoped β -boron. The cell dimensions were determined from a least squares fitting of measurements of 2θ angles for 21 reflections.

Intensities were recorded in the $\theta - 2\theta$ scanning mode up to $2\theta = 65^\circ$ for $\text{VB}_{\sim 65}$ with $h = 0$ to $+17$, $k = -17$ to $+17$, $l = -37$ to $+37$ resulting in a total of 5437 measured intensities. For $\text{VB}_{\sim 165}$ 3064 intensities were recorded up to a maximum 2θ of 50° for $h = 0$ to $+14$, $k = -14$ to $+14$, and $l = -29$ to $+29$. Background intensities on each side of the scanning interval were measured and two standard reflections were recorded after every 50 regular measurements. The absorption coefficients were very low (5.43 cm^{-1} for $\text{VB}_{\sim 65}$ and 2.65 cm^{-1} for $\text{VB}_{\sim 165}$, and no absorption corrections were applied.

The data processing and crystallographic computations were made with the SHELXTL package of programs (8).

Structure Refinement

After the reduction of the intensities to F values, rejection of those structure factors which were less than $4\sigma(F)$, and an averaging of equivalent reflections the number of independent structure factors were 1055 for $\text{VB}_{\sim 65}$ and 543 for $\text{VB}_{\sim 165}$.

The coordinates and temperature factors of boron atoms in β -boron (9) were used to calculate a difference Fourier synthesis, which clearly indicated the presence of vanadium atoms in A(1) and D sites (notation used in Ref. (2)) for $\text{VB}_{\sim 65}$; vanadium atoms were found only in A(1) sites for $\text{VB}_{\sim 165}$. The atomic coordinates, tempera-

ture factors and occupational parameters were refined by minimizing the function $\Sigma W(F_o - F_c)^2$ by a least-squares procedure. The weighting function (W) was $1/[\sigma^2(F) + (G(F))^2]$ with $G = 0.00008$ for $\text{VB}_{\sim 65}$ and $G = 0.00042$ for $\text{VB}_{\sim 165}$. The residual indices are defined as

$$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|,$$

and

$$R_w = \frac{\Sigma W(|F_o| - |F_c|)^2}{\Sigma W|F_o|^2} \quad (1)$$

Results

$\text{VB}_{\sim 65}$

The refined atomic coordinates and occupancy factors are given in Table I and the anisotropic temperature factors in Table II. The residuals are: $R = 0.054$ and $R_w = 0.051$. Notable is the absence of any elec-

TABLE I
ATOM COORDINATES ($\times 10^4$) FOR $\text{VB}_{\sim 65}$

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>
B(1)	36(i)	1762(2)	1761(2)	1768(1)
B(2)	36(i)	3191(2)	2960(2)	1288(1)
B(3)	36(i)	2611(2)	2169(2)	4196(1)
B(4)	36(i)	2357(2)	2516(2)	3469(1)
B(5)	18(h)	0547(1)	1095(2)	-0558(1)
B(6)	18(h)	0864(1)	1728(2)	0132(1)
B(7)	18(h)	1105(1)	2211(2)	-1132(1)
B(8)	18(h)	1700(1)	3401(2)	0279(1)
B(9)	18(h)	1295(1)	2590(2)	-2340(1)
B(10)	18(h)	1022(1)	2044(2)	-3018(1)
B(11)	18(h)	0565(1)	1130(2)	3268(1)
B(12)	18(h)	0898(1)	1796(2)	3986(1)
B(13) ^a	18(h)	0564(2)	1128(4)	-4457(1)
B(14)	6(c)	0	0	3856(2)
B(15)	3(b)	0	0	5000
B(16)	18(h)	Vacant		
V(1) ^b	6(c)	0	0	1342(1)
V(2) ^c	18(h)	1990(4)	3980(7)	1738(3)

Note. All sites, except for B(16) and the three listed ones, are fully occupied.

^a Occupancy 74.6%.

^b Occupancy 64.0%.

^c Occupancy 5.3%.

TABLE II
ANISOTROPIC TEMPERATURE FACTORS ($\text{\AA}^2 \times 10^3$)
FOR VB₋₆₅

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B(1)	7(1)	6(1)	6(1)	1(1)	1(1)	4(1)
B(2)	7(1)	6(1)	5(1)	-1(1)	-0(1)	3(1)
B(3)	4(1)	5(1)	7(1)	-0(1)	-0(1)	2(1)
B(4)	5(1)	5(1)	6(1)	-0(1)	-0(1)	3(1)
B(5)	4(1)	4(1)	6(1)	-0(1)	-0(1)	2(1)
B(6)	5(1)	4(1)	5(1)	0(1)	0(1)	2(1)
B(7)	5(1)	6(1)	6(1)	-1(1)	-0(1)	3(1)
B(8)	5(1)	6(1)	6(1)	1(1)	0(1)	3(1)
B(9)	5(1)	5(1)	6(1)	-0(1)	-0(1)	2(1)
B(10)	4(1)	4(1)	5(1)	-0(1)	-0(1)	2(1)
B(11)	5(1)	4(1)	4(1)	0(1)	0(1)	2(1)
B(12)	5(1)	4(1)	6(1)	-1(1)	-0(1)	2(1)
B(13)	17(1)	10(2)	12(2)	-1(1)	-0(1)	5(1)
B(14)	9(1)	9(1)	4(2)	0	0	5(1)
B(15)	5(1)	5(1)	5(1)	0	0	3(1)
V(1)	3(1)	3(1)	3(1)	0	0	1(1)
V(2)	7(3)	5(3)	20(4)	3(3)	1(1)	3(2)

Note. The anisotropic temperature factor exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \dots + 2hka^*b^*U_{12})$.

iron density in the B(16) site, which has an occupancy of $\sim 25\%$ in β -rhombohedral boron. A final $|F_o| - |F_c|$ synthesis had no peaks greater than 5% of that of a boron atom.

VB₋₁₆₅

The atomic coordinates and isotropic temperature factors are given in Table III. The residuals are: $R = 0.049$ and $R_w = 0.069$. The coordinates are the same within the standard deviation as for VB₋₆₅. There is partial occupancy of the B(16) site, which is also partially occupied in β -rhombohedral boron. Vanadium is found only at the A(1) site. The highest density in a $|F_o| - |F_c|$ synthesis corresponded to 8% of a boron peak and was in the vicinity of a V(2) site, but it was quite diffuse.

Discussion

The occurrence of vanadium in β -rhombohedral boron resembles that of chro-

mium (2) and iron (3). For these three elements the only sites occupied by metal atoms are A(1) and D. The boron framework is essentially the same in all three cases and the interatomic distances (Tables IV and V) are generally similar. Some differences do occur, however, around the impurity sites.

For the A(1) site, we find that the average distance from the V atom to the surrounding twelve boron atoms [$6B(1) + 3B(5) + 3B(7)$] increases with increasing fractional occupancy. Our present results for V are shown in Fig. 1, and are compared to those found for undoped β -boron (10), Cu (11, 12), Ge (13), Mn (11), Ni (14), Si (15), Fe (3), and Cr (2). The error bars represent the uncertainty in the measured average

TABLE III
ATOM COORDINATES ($\times 10^4$) AND TEMPERATURE
FACTORS ($\text{\AA}^2 \times 10^3$) FOR VB₋₁₆₅

Atom	x	y	z	U_{eq}^a
B(1)	1746(2)	1752(2)	1769(1)	7(1)
B(2)	3190(2)	2962(2)	1291(1)	6(1)
B(3)	2612(2)	2171(2)	4196(1)	7(1)
B(4)	2353(2)	2515(2)	3469(1)	6(1)
B(5)	0545(2)	1089(3)	-0560(1)	6(1)
B(6)	0866(2)	1731(3)	0132(1)	5(1)
B(7)	1101(2)	2202(3)	-1136(1)	6(1)
B(8)	1702(2)	3404(3)	0277(1)	6(1)
B(9)	1292(2)	2584(3)	-2337(1)	7(1)
B(10)	1021(2)	2042(3)	-3016(1)	5(1)
B(11)	0565(2)	1131(3)	3268(1)	5(1)
B(12)	0898(2)	1797(3)	3989(1)	6(1)
B(13) ^b	0575(3)	1151(5)	-4462(2)	14(2)
B(14)	0	0	3855(2)	6(1)
B(15)	0	0	5000	15(2)
B(16) ^c	0539(13)	1079(26)	1182(10)	16(9)
V(1) ^d	0	0	1343(1)	1(1)
V(2)	Vacant			

Note. All sites, except for V(2) and the three listed ones, are fully occupied.

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

^b Occupancy 76.3%.

^c Occupancy 14.7%.

^d Occupancy 31.6%.

distance. The average distance extrapolates to 2.183(4) Å for a fully occupied A(1) site. Thus, the radial expansion of the A(1) site is a maximum of 0.044 Å independent of which atom or ion enters the site. This expansion is much less than the radius of any of the atoms or ions mentioned, and indicates that they enter a pre-existing hole in the structure. We conclude that V doping of

the A(1) site is not substantially different from that of other transition metals.

For the V(2) or D site, we find that the average V(2)-B distance is 2.403(3) Å. Here there are 14 fully occupied boron sites:

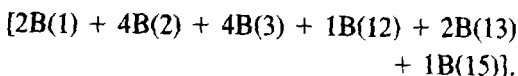


TABLE IV
INTERATOMIC DISTANCES IN VB_{-65} (IN Å)

B(1)- B(1)	1.931(3)	B(6) -2B(5)	1.763(2)	B(13)-2B(3)	1.810(2)
- B(1)	1.934(3)	- B(5)	1.756(3)	-2B(12)	1.870(3)
- B(2)	1.855(2)	-2B(6)	1.759(4)	-2B(13)	1.856(4)
- B(2)	1.836(2)	- B(8)	1.628(3)	- B(14)	1.791(5)
- B(7)	1.853(3)	B(7) -2B(1)	1.853(3)	- B(15)	1.683(3)
- B(9)	1.849(3)	-2B(2)	1.803(2)	-2V(2)	2.491(7)
- V(1)	2.185(1)	- B(5)	1.733(3)	- V(2)	2.086(8)
- V(2)	2.321(7)	- B(9)	1.804(3)	B(14)-3B(11)	1.771(4)
B(2)- B(1)	1.836(2)	- V(1)	2.160(2)	3B(12)	1.734(2)
- B(1)	1.855(2)	B(8) -2B(3)	1.798(3)	-3B(13)	1.791(5)
- B(2)	1.829(3)	-2B(4)	1.737(3)	B(15)-6B(13)	1.683(3)
- B(3)	1.728(2)	- B(6)	1.628(3)	-6V(2)	2.559(4)
- B(7)	1.803(2)	- B(10)	1.834(3)	V(1) -6B(1)	2.185(1)
- B(9)	1.857(4)	B(9) -2B(1)	1.849(3)	-3B(5)	2.143(2)
- V(2)	2.370(5)	-2B(2)	1.857(2)	-3B(7)	2.160(2)
- V(2)	2.386(5)	- B(7)	1.804(3)	-3V(2)	3.898(3)
B(3)- B(2)	1.728(2)	- B(10)	1.703(3)	V(2) -2B(1)	2.321(7)
- B(3)	1.896(3)	B(10)-2B(4)	1.846(2)	-2B(2)	2.370(5)
- B(4)	1.829(2)	- B(8)	1.834(3)	-2B(2)	2.386(5)
- B(8)	1.798(3)	- B(9)	1.703(3)	-2B(3)	2.298(7)
- B(12)	1.784(2)	-2B(11)	1.788(2)	-2B(3)	2.474(6)
- B(13)	1.810(2)	B(11)-2B(4)	1.850(2)	- B(12)	2.407(8)
- V(2)	2.298(7)	-2B(10)	1.788(2)	-2B(13)	2.491(4)
- V(2)	2.474(6)	-2B(11)	1.860(3)	- B(13)	2.086(7)
B(4)- B(3)	1.829(2)	- B(12)	1.831(3)	- B(15)	2.559(4)
- B(4)	1.683(3)	- B(14)	1.771(4)	-2V(2)	2.576(8)
- B(8)	1.737(3)	B(12)-2B(3)	1.784(2)	- V(1)	3.898(3)
- B(10)	1.846(2)	-2B(4)	1.858(2)		
- B(11)	1.850(2)	- B(11)	1.831(3)		
- B(12)	1.858(2)	-2B(13)	1.870(3)		
B(5)-2B(5)	1.802(3)	- B(14)	1.734(2)		
-2B(6)	1.763(2)	- V(2)	2.407(8)		
- B(6)	1.756(3)				
- B(7)	1.733(3)				
- V(1)	2.143(2)				

TABLE V
 INTERATOMIC DISTANCES IN VB₋₁₆₅ (IN Å)

B(1)– B(1)	1.905(3)	B(6) –2B(5)	1.763(3)		
– B(1)	1.924(3)	– B(5)	1.758(4)	B(12)–2B(3)	1.779(3)
– B(2)	1.845(3)	–2B(6)	1.758(4)	–2B(4)	1.854(3)
– B(2)	1.860(3)	– B(8)	1.623(4)	– B(11)	1.831(4)
– B(7)	1.840(4)			–2B(13)	1.872(4)
– B(9)	1.841(4)	B(7) –2B(1)	1.840(4)	– B(14)	1.734(3)
– B(16)	1.808(20)	–2B(2)	1.804(3)		
– V(1)	2.167(2)	– B(5)	1.732(4)	B(13)–2B(3)	1.795(3)
		– B(9)	1.814(4)	–2B(12)	1.872(4)
B(2)– B(1)	1.845(3)	–2B(16)	1.812(12)	–2B(13)	1.890(5)
– B(1)	1.860(3)	– V(1)	2.145(3)	– B(14)	1.812(6)
– B(2)	1.813(4)			– B(15)	1.685(4)
– B(3)	1.723(3)	B(8) –2B(3)	1.795(4)		
– B(7)	1.804(3)	–2B(4)	1.734(3)	B(14)–3B(11)	1.762(5)
– B(9)	1.857(4)	– B(6)	1.623(4)	–3B(12)	1.734(3)
		– B(10)	1.830(4)	–3B(13)	1.812(6)
B(3)– B(2)	1.723(3)				
– B(3)	1.894(4)	B(9) –2B(1)	1.841(4)	B(15)–6B(13)	1.685(4)
– B(4)	1.824(3)	–2B(2)	1.857(4)		
– B(8)	1.795(4)	– B(7)	1.814(4)	B(16)– B(1)	1.808(20)
– B(12)	1.779(3)	– B(10)	1.700(4)	–2B(5)	1.806(24)
– B(13)	1.795(3)			–2B(7)	1.812(12)
		B(10)–2B(4)	1.844(3)	–2B(16)	1.772(28)
B(4)– B(3)	1.824(3)	– B(8)	1.830(4)		
– B(4)	1.682(4)	– B(9)	1.700(4)	V(1) –6B(1)	2.167(2)
– B(8)	1.734(3)	– B(9)	1.700(4)	–3B(5)	2.133(4)
– B(10)	1.844(3)	–2B(11)	1.785(4)	–3B(7)	2.145(3)
– B(11)	1.841(3)				
– B(12)	1.854(3)	B(11)–2B(4)	1.841(3)		
		–2B(10)	1.785(4)		
B(5)–2B(5)	1.789(3)	–2B(11)	1.857(4)		
–2B(6)	1.763(3)	– B(12)	1.831(4)		
– B(6)	1.758(4)	– B(14)	1.762(5)		
– B(7)	1.732(4)				
– B(16)	1.805(24)				
– V(1)	2.133(4)				

In calculating the average distance, we have assumed that the partially occupied B(13) site at the short distance of 2.086 Å is empty and all others are fully occupied. In undoped β -boron, the average distance from the center of the D site at position $x = 0.2020$, $y = 2x$, $z = 0.1735$ to the surrounding boron atoms is 2.393(4) Å from the data of Callmer (10). The D site expansion for V and for the other impurities Cr (2), Fe (3), Sc (16), and Mn (11) is given in Fig. 2. We see that, again, V falls close to the curve for

the other transition metals within the limits of error. At low fractional occupancy, the average hole size is not much greater than in undoped β -boron.

Even though the fractional occupancy of the D site is low for VB₋₆₅, we find the V(2)–B(15) distance to be 2.559(4) Å. This is noticeably larger than for any other D site impurities shown in Fig. 2, and larger than the 2.491(4) Å in undoped β -boron. The reason for this difference is not clear, but it is significantly greater than the stated un-

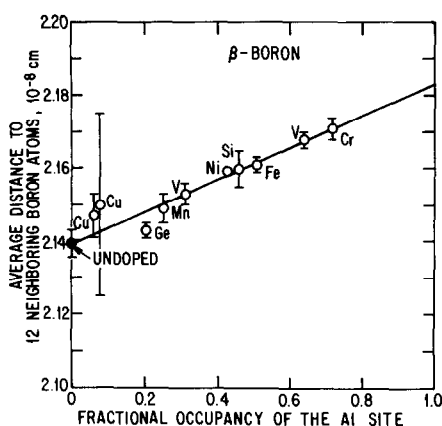


FIG. 1. The average impurity-boron distance for the A(1) site in β -boron as a function of the fractional occupancy.

certainty in the bond distance. Other studies (14) have found that the D site coordination is quite variable.

There are two boron-atom sites in undoped β -boron that are not fully occupied (10). As the transition metal content increases, the occupancy of the B(13) site does not change, while the boron occupancy of the interstitial B(16) site correlates inversely with the occupancy of the A(1) site.

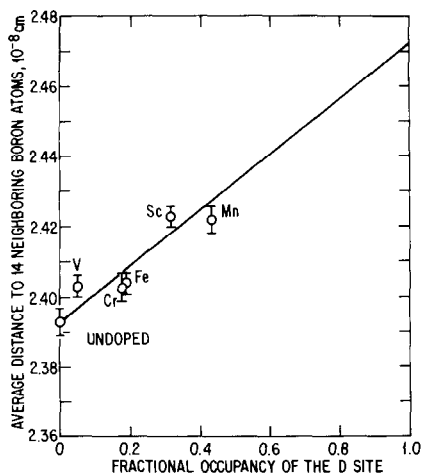


FIG. 2. The average impurity-boron distance for the D site in β -boron as a function of the fractional occupancy. Fractional occupancies greater than 0.5 are unknown.

TABLE VI
PERCENTAGE OCCUPATION OF PARTIALLY OCCUPIED SITES IN β -BORON STRUCTURES

Site	CrB ₋₄₁ (2)	FeB ₋₄₉ (3)	VB ₋₆₅	VB ₋₁₆₅	β -Boron (10)
M(1), A(1)	71.9(6)%	50.7(3)	64.0(4)	31.6(4)	—
M(2), D	18.0(3)%	18.5(2)	5.3(2)	<2.3	—
B(13)	71.7(18)%	72.1(11)	74.6(12)	76.3(14)	73.4(15)
B(16)	0%	0	0	14.7(16)	24.8(16)

The A(1) site is only 1.135 Å away from the nearest B(16) site in undoped β -boron, and there is competition in their occupancy. Table VI summarizes the data for the occupancy of the various sites.

The B-to-V ratio for each sample has been calculated from the occupancy factors of the various atomic positions as listed in Tables I and III. For example, in the hexagonal cell in Table I, there are 310.4 boron atoms and 4.79 vanadium atoms. Their abundance ratio is thus 64.8. We give the composition as VB₋₆₅. From Table III, the abundance ratio for the second sample is 165.3.

The volume of the β -boron unit cell generally increases as the interstitial impurity content increases. This has been studied for Cu (17) in detail and partially for many other impurities (1, 18) as well. The data for Cu shows that the expansion is not exactly linear with increasing Cu content because the impurity site preference is a function of concentration. We have studied this cell expansion for V as shown in Fig. 3. Here VB₋₁₆₅ is sample 66 and VB₋₆₅ is sample 91. Two other samples of rapidly-cooled boron, 73 and 136, were also studied. A variety of different X-ray machines were used as noted, with N = Nicolet P3F diffractometer (7), GA = Gandolfi camera (19) with a General Electric XRD-4 X-ray generator, and R = Rigaku Theta-Theta diffractometer (20). In all cases, undoped β -boron grown from the melt was also measured in order to obtain an accurate zero-concentra-

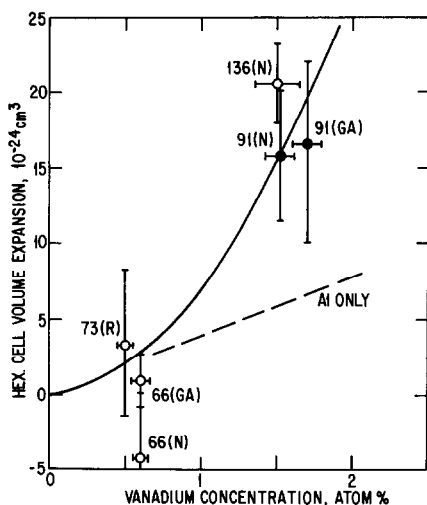


FIG. 3. The volume expansion of the hexagonal unit cell in β -boron at room temperature as a function of the vanadium content. The open circles are rapidly cooled samples; the closed circles are slowly cooled samples.

tion volume. Note that the results for V appear to be nonlinear and that the dashed line labeled A(1) may be the behavior when only A(1) sites are being occupied.

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