

The Crystal Structure of $\text{CuVO}_3(\text{II})$, a High-Pressure Ilmenite Phase

J. R. REA* AND E. KOSTINER†

Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14850

Received September 18, 1972

The crystal structure of a second high-pressure copper vanadate phase, $\text{CuVO}_3(\text{II})$, has been determined and refined by full-matrix least-squares procedures using automatic diffractometer data to a residual $R = 0.042$ ($R_w = 0.051$). The space group is rhombohedral, $R\bar{3}$, with hexagonal unit cell $a = 4.966(2)$ and $c = 14.084(5)$ Å [$a_R = 5.501(2)$ Å and $\alpha = 53.66(3)^\circ$]. The structure is the fully ordered ilmenite-type and, on the basis of published magnetic data and the interatomic distances, the valence distribution $\text{Cu}^+\text{V}^{5+}\text{O}_3$ is proposed. This represents a unique example of Cu^+ in an octahedral environment.

Introduction

Chamberland (1) suggested that the two high-pressure phases of copper vanadate, $\text{CuVO}_3(\text{I})$ and $\text{CuVO}_3(\text{II})$, prepared by him were related to the rhombohedral ilmenite structure-type because of the similarities in the powder X-ray diffraction patterns among the three compounds. We have recently confirmed by a single-crystal X-ray structural analysis (2) that $\text{CuVO}_3(\text{I})$ is a triclinic distortion of the ilmenite structure-type with ionic distribution $\text{Cu}^{2+}\text{V}^{4+}\text{O}_3$. In this paper we report the results of a similar investigation of $\text{CuVO}_3(\text{II})$, which is found to have the undistorted ordered ilmenite structure with Cu^+ in an octahedral environment.

Experimental Methods

Small single crystals of $\text{CuVO}_3(\text{II})$ were generously supplied by Professor B. L. Chamberland. Their preparation at 65 kbar and 900–1000°C has been described (1). An irregularly shaped crystal was selected; precession photographs confirmed the symmetry to be rhombohedral.

The lattice parameters were determined in a PICK-II least-squares refinement program,

* Present address: Mary Baldwin College, Staunton, VA.

† Author to whom correspondence should be addressed at Department of Chemistry and Institute of Materials Science, University of Connecticut, Storrs, CT 06268.

using 34 reflections within the angular range $11^\circ < |2\theta| < 29^\circ$; the reflections were manually centered on a Picker FACS-I four-circle diffractometer using $\text{MoK}\alpha$ radiation. At 22°C the lattice parameters for the triply primitive hexagonal unit cell are $a = 4.966(2)$ and $c = 14.084(5)$ Å; the parameters for the rhombohedral unit cell are $a = 5.501(2)$ Å and $\alpha = 53.66(3)^\circ$. The numbers in parentheses represent the standard deviations in the last reported figure. These parameters are in substantial agreement with those derived from the refined powder diffraction data (1). The calculated density is 5.381 g/cm³ ($V_R = 100.3$ Å³).

Diffraction intensities were measured using Zr-filtered $\text{MoK}\alpha$ radiation at a takeoff angle of 2.5° with the diffractometer operating in the θ - 2θ scan mode. Scans were made at 1° per min over 1.5° with allowance for dispersion, and with 40-sec background counts taken at both ends of the scan. Of the 309 independent data investigated in the angular range $2\theta < 71^\circ$, a total of 298 were considered observable according to the criterion $|F_o| > 0.675\sigma_F$, where σ_F is defined as $0.02|F_o| + [C + k^2B]^{1/2}/2|F_o|Lp$; the total scan count is C , k is the ratio of scanning time to the total background count time, and B is the total background count. Three reflections were systematically monitored, and no random variations in intensity greater than 3.5% were observed over the entire data collection period; the mean variation was very much smaller. However,

TABLE I
OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	F OBS	FCAL	H	K	L	F OBS	FCAL	H	K	L	F OBS	FCAL	H	K	L	F OBS	FCAL
-6	7	5	91	100	-1	3	20	448	412	0	2	22	287	285	1	2	5	29	13
-6	7	8	365	375	-1	4	1	145	151	0	3	0	2621	2287	1	2	8	808	815
-5	6	4	865	893	-1	4	4	1072	1065	0	3	3	177	173	1	2	11	311	314
-5	6	7	139	126	-1	4	7	277	242	0	3	6	593	568	1	2	14	966	983
-5	6	10	591	590	-1	4	10	1139	1130	0	3	9	45	52	1	2	17	92	82
-5	6	13	54	72	-1	4	13	109	103	0	3	12	41	44	1	2	20	416	411
-5	7	3	132	167	-1	4	16	137	119	0	3	15	284	288	1	3	1	45	32
-5	7	6	451	465	-1	4	19	70	63	0	3	18	718	718	1	3	4	1429	1358
-5	7	9	170	162	-1	5	0	1015	1056	0	4	-1	62	61	1	3	7	329	323
-5	8	2	77	85	-1	5	3	53	62	0	4	2	454	420	1	3	10	912	899
-4	5	3	70	50	-1	5	6	824	827	0	4	5	78	53	1	3	13	124	116
-4	5	6	842	843	-1	5	9	71	53	0	4	8	816	774	1	3	16	287	281
-4	5	9	53	38	-1	5	12	310	293	0	4	11	167	162	1	3	19	85	85
-4	5	15	145	149	-1	5	15	181	162	0	4	14	727	710	1	4	0	1143	1036
-4	6	2	342	365	-1	6	-1	135	143	0	5	-2	150	121	1	4	3	350	337
-4	6	5	117	123	-1	6	2	228	231	0	5	1	277	263	1	4	6	775	746
-4	6	8	626	622	-1	6	8	487	483	0	5	4	1052	985	1	4	9	265	249
-4	6	11	72	29	-1	6	11	80	26	0	5	7	62	69	1	4	12	153	157
-4	6	14	553	571	-1	6	14	646	630	0	5	10	744	728	1	4	15	52	41
-4	7	1	24	36	-1	7	-2	321	346	0	5	13	100	89	1	5	-1	37	19
-4	7	4	535	566	-1	7	1	47	36	0	6	-3	28	26	1	5	8	437	432
-4	7	7	59	107	-1	7	4	447	475	0	6	0	1049	968	1	5	11	171	169
-4	7	10	727	735	-1	7	7	101	84	0	6	3	58	61	1	5	14	649	637
-4	8	3	34	27	0	0	3	146	153	0	6	6	408	380	1	6	-2	112	111
-3	4	2	253	297	-2	6	13	141	119	0	7	2	251	218	1	6	1	120	99
-3	4	5	71	62	0	0	9	154	143	1	0	1	172	165	1	6	4	772	737
-3	4	8	750	733	0	12	128	122	1	0	4	2116	2149	1	6	7	142	144	
-3	4	11	256	289	-2	7	6	481	492	0	7	387	399	2	0	2	360	354	
-3	4	14	817	810	-2	7	9	151	157	0	10	1415	1480	2	0	5	306	294	
-3	4	17	104	103	-1	2	3	414	388	0	10	13	66	64	2	0	8	888	882
-3	5	1	286	301	-1	2	6	1751	1734	1	0	16	247	253	2	0	11	193	190
-3	5	4	1078	1091	-1	2	9	219	216	0	1	8	1161	1213	1	0	14	1089	1107
-3	5	10	865	861	-1	2	12	538	553	0	1	11	283	291	1	0	20	384	383
-3	5	13	87	73	-1	2	15	308	296	0	1	14	1037	1082	2	1	31	317	336
-3	5	16	163	159	-1	2	18	487	448	0	1	20	479	480	2	1	4	1419	1494
-3	6	3	54	51	0	2	1	482	432	1	1	6	1349	1432	2	1	7	176	182
-3	6	6	421	432	-1	2	4	2038	1961	1	1	9	553	582	2	1	10	1209	1263
-3	6	9	83	22	-1	3	5	277	274	0	2	7	144	138	1	1	13	40	8
-3	6	15	185	185	-1	3	8	937	936	1	1	12	229	239	2	1	16	172	167
-3	7	2	184	183	0	2	10	1232	1268	1	1	15	698	715	2	1	19	139	142
-3	7	5	51	29	-1	3	11	131	124	0	2	13	45	62	1	1	22	1371	1378
-3	7	8	445	451	-1	3	17	200	202	0	2	19	291	288	2	2	3	116	120

2	2	6	1086	1106	2	5	6	541	527	3	2	10	762	793	4	0	16	167	177	5	0	8	425	411
2	2	9	115	110	2	5	9	27	26	3	2	13	46	23	4	1	3	332	347	5	0	11	48	30
2	2	12	387	384	3	0	3	187	159	3	2	16	212	219	4	1	6	722	725	5	0	14	770	793
2	2	15	208	220	3	0	6	603	570	3	3	0	1206	1192	4	1	9	252	254	5	1	4	722	760
2	2	18	411	405	3	0	9	62	62	3	3	3	96	94	4	1	12	140	140	5	1	7	68	31
2	3	2	218	205	3	0	12	66	42	3	3	6	435	424	4	2	2	146	134	5	1	10	708	726
2	3	5	245	240	3	0	15	288	294	3	3	12	60	18	4	2	5	93	106	5	1	13	35	19
2	3	8	521	528	3	0	18	691	715	3	3	15	155	158	4	2	8	447	468	5	2	3	35	52
2	3	11	42	40	3	1	2	543	566	3	4	2	350	344	4	2	11	230	240	5	2	6	520	548
2	3	14	820	837	3	1	5	165	153	3	4	5	57	71	4	3	1	615	645	5	2	9	56	8
2	4	1	114	104	3	1	8	874	899	3	4	8	571	573	4	3	1	40	36	5	3	2	77	66
2	4	4	739	706	3	1	11	110	106	3	4	11	59	25	4	3	4	721	739	6	0	6	371	388
2	4	7	106	105	3	1	14	712	731	3	5	1	132	123	4	3	7	126	127	6	0	9	57	9
2	4	10	833	834	3	1	17	68	43	4	0	4	1098	1068	4	3	10	548	579	6	1	5	71	83
2	4	13	87	88	3	2	1	172	181	4	0	7	263	252	4	4	0	608	620	6	1	8	510	548
2	5	0	822	772	3	2	4	1211	1155	4	0	10	966	963	4	4	3	79	88					
2	5	3	73	67	3	2	7	54	75	4	0	13	121	115	5	0	5	197	208					

two scale factors were used in the refinements, since portions of the data were taken at two different times.

The intensity data were corrected for Lorentz and polarization effects, and absorption corrections were made. Since the crystal was irregularly shaped, the absorption corrections were made using a computer program written by N. W. Alcock and modified by B. Lee for a crystal of general shape. Input for the program included the indices of the plane faces of the crystal, which were closely approximated with the aid of precession photographs, and the orientation angles of the crystal coordinate system with respect to the diffractometer coordinate system, which were obtained from the program PICK-II. The maximum relative absorption correction applied was 13% of $|F_o|$.

Determination and Refinement of the Structure

The space group of $\text{CuVO}_3(\text{II})$ was reported to be $R\bar{3}m$ (1). However, precession photographs were carefully examined, and the true Laue symmetry was found to be $\bar{3}$, allowing the possible space groups $R\bar{3}$ or $R\bar{3}$. Analysis of the Patterson map revealed more than one possible set of positions for the copper and vanadium atoms on the hexagonal c -axis. The best set was determined by a series of least-squares refinements, and a difference Fourier map clearly revealed the oxygen sites.

Three cycles of least-squares refinement (4) in the space group $R\bar{3}$ (the space group of the ilmenite structure-type), using a $1/\sigma^2$ weighting scheme, zerovalent scattering factors for Cu, V, and O (5), isotropic temperature factors, and corrections for secondary extinction and anomalous dispersion yielded a residual $R = 0.054$ and a weighted residual $R_w = 0.065$. Since $\text{CuVO}_3(\text{II})$ was reported to be nonstoichiometric (1), an anisotropic refinement was run

in which the occupancies of the vanadium and oxygen sites were allowed to vary. The occupancies did not deviate significantly from 100%, and R was not lower than R for fixed occupancies. Furthermore, the final difference Fourier map was flat, except for minor background. This indicates a fully ordered ilmenite structure. The final anisotropic refinement (occupancies fixed at 100%), based on a data:parameter ratio of 16.5 with 18 independently varied parameters, yielded a final $R = 0.042$ and $R_w = 0.051$ for the observed data. Calculated and observed structure factors are listed in Table I. In the final refinement the maximum extinction correction (6) was 7% of $|F_c|$ for the 104 reflection.

Table II presents the final atomic coordinates and anisotropic thermal parameters.

Discussion

$\text{CuVO}_3(\text{II})$ has the ordered ilmenite structure. The ilmenite structure can be described (7) as a hexagonal close-packed array of oxygen ions with metal ions occupying two-thirds of the octahedral holes. The different metal ions are in alternating layers such that each octahedron containing a copper ion shares a face with a vanadium octahedron above or below it (but not both) and also share edges with three other copper octahedra in the same layer. Vanadium octahedra have similar linkages. This means that the octahedral holes of the oxygen array, which are linked by face-sharing into chains parallel to the hexagonal c -axis, are filled in the sequence vacancy-Cu-V-vacancy-V-Cu-vacancy, etc. As in $\text{CuVO}_3(\text{I})$, the unlike metal ions in the face-sharing octahedra repel each other so that they are further apart (2.998(2) Å) than the like metals of edge-sharing octahedra within a layer (2.951(1) Å for Cu; 2.930(1) Å for V).

TABLE II
FRACTIONAL ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS^a

Atom	10^4x	10^4y	10^4z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0	0	1418.3(5)	0.59(2)	B_{11}	1.02(3)	$\frac{1}{2}B_{11}$	0	0
V	0	0	3547.1(6)	0.44(2)	B_{11}	0.65(3)	$\frac{1}{2}B_{11}$	0	0
O	3704(5)	80(5)	765(1)	0.65(7)	0.43(7)	0.74(7)	0.27(6)	0.12(5)	0.04(5)

^a Numbers in parentheses are estimated standard deviations in the last significant figure.

TABLE III
BOND DISTANCES, BOND ANGLES, AND POLYHEDRAL EDGE LENGTHS^a

	Distance (Å)	Angle (°)	Edge length (Å)
i. Copper polyhedron ^b			
3x Cu-O	2.039(2)		
3x Cu-O'	2.241(2)		
3x O-Cu-O		101.2(1)	3.152(4)
3x O-Cu-O'		93.0(1)	3.107(4)
3x O-Cu-O'		89.2(1)	3.008(3)
3x O'-Cu-O'		73.5(1)	2.682(4)
3x O-Cu-O'		160.3(1)	4.216(2)
ii. Vanadium polyhedron ^b			
3x V-O	1.788(2)		
3x V-O'	2.073(2)		
3x O-V-O		102.6(1)	2.790(4)
3x O-V-O'		81.6(1)	2.531(4)
3x O-V-O'		93.6(1)	2.820(4)
3x O'-V-O'		80.6(1)	2.682(4)
3x O-V-O'		161.9(1)	3.814(3)
iii. Oxygen polyhedron			
V-O-Cu		120.9(1)	3.331(1)
V-O-V'		98.4(1)	2.930(1)
V-O-Cu'		135.8(1)	3.737(1)
Cu-O-V'		126.7(1)	3.675(1)
Cu-O-Cu'		87.0(1)	2.951(1)
V'-O-Cu'		88.0(1)	2.998(2)
iv. Metal-metal distances			
3x Cu-Cu' (in plane)	2.951(1)		
Cu'-V' (face sharing)	2.998(2)		
3x Cu-V (edge sharing)	3.331(1)		
3x V-V' (in plane)	2.930(1)		

^a Numbers in parentheses are estimated standard deviations in the last figure.

^b The primed and unprimed oxygen atoms belong to different close-packed layers.

The fact that $\text{CuVO}_3(\text{II})$ exhibits Van Vleck paramagnetism (1) implies that the molecular species in their ground states have no paramagnetic moment. Therefore, Cu and V in this compound exist in d^{10} and d^0 configurations, respectively; that is, the valence distribution is $\text{Cu}^+\text{V}^{5+}\text{O}_3$. Analysis of bond distances supports this argument to some extent. Table III lists bond distances, angles, and polyhedral edge lengths. The average Cu-O and V-O bond lengths are 2.140 and 1.931 Å, respectively. Using the ionic radius for four-coordinated oxygen (1.38 Å) derived by Shannon and Prewitt (8), the ionic radii for copper and vanadium in $\text{CuVO}_3(\text{II})$ are 0.76 and 0.55 Å, res-

pectively. For $\text{Cu}^{2+}\text{V}^{4+}\text{O}_3(\text{I})$ the ionic radii for Cu and V were found to be 0.75 and 0.56, respectively. Although the derived ionic radii in these two compounds are not markedly different, we believe, considering the accuracy of the data, that this slight difference supports the lower valence state for copper (larger ionic size) and higher valence state for vanadium (smaller size) in $\text{CuVO}_3(\text{II})$ —that is, the d^{10} - d^0 configuration implied by the magnetic data.

The formation of the ilmenite-related vanadate phases is apparently related to the valence state of the vanadium involved. Each of the four triclinic high pressure phases $\text{MVO}_3(\text{I})$ (M = Co, Cu, Ni, Mn) contains vanadium as V^{4+} (1, 2, 9,

10). The only one of these which forms a second (undistorted) high pressure ilmenite phase is CuVO_3 , in which the copper atom can exist as a stable univalent cation thereby allowing vanadium to occur as V^{5+} , and which seems to have the unique feature of Cu^+ in an octahedral site.

Acknowledgments

We acknowledge helpful discussions with Professor B. L. Chamberland (University of Connecticut). This work was supported in part by the Advanced Research Projects Agency through the Materials Science Center, Cornell University.

References

1. B. L. CHAMBERLAND, *J. Solid State Chem.* **1**, 138 (1970).
2. J. R. REA, P. W. BLESS AND E. KOSTINER, *J. Solid State Chem.* **5**, 446 (1972).
3. "International Tables for X-Ray Crystallography", Mathematical Tables, Vol. 2, p. 295. Kynoch, Birmingham, England (1968).
4. W. R. BUSING, K. O. MARTIN AND H. A. LEVY, Oak Ridge National Laboratory, ORNL-TM-305. Oak Ridge, TN (1962).
5. D. T. CROMER AND J. B. MANN, *Acta Crystallogr., Sect. A* **24**, 321 (1968).
6. W. H. ZACHARIASEN, *Acta Crystallogr.* **23**, 558 (1967); *Sect. A* **24**, 324 (1968).
7. G. SHIRANE, S. J. PICKART, R. NATHANS AND Y. ISHIKAWA, *J. Phys. Chem. Solids* **10**, 35 (1959).
8. R. D. SHANNON AND C. T. PREWITT, *Acta Crystallogr., Sect. B* **25**, 925 (1969).
9. B. L. CHAMBERLAND, *J. Solid State Chem.* **2**, 521 (1970).
10. Y. SYONO, S. AKIMOTO AND Y. ENDOH, *J. Phys. Chem. Solids* **32**, 243 (1971).