The Crystal Structure of α-Copper Vanadate

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The crystal structure of α-copper vanadate has been determined and refined by full-matrix least-squares procedures using automatic diffractometer data to a residual $R = 0.050$ ($R_w = 0.059$). The space group is rhombohedral, $R\bar{3}$, with hexagonal unit cell $a = 12.857(3)$ and $c = 7.161(2)$ Å ($a_R = 7.797(2)$ Å and $\alpha = 111.06(1)°$). On the basis of the detailed structural analysis the contents $Cu_{7-x}V_6O_{19-x}$ with $x = 0.22$ are proposed for the rhombohedral cell. Copper is in the divalent and vanadium in the quadrivalent state. The structure is based on a cubic close-packed array of oxygen ions with the vanadium ion occupying an octahedral site, one copper in a partially occupied octahedral site and the other copper in a tetrahedral site. The latter is one of the few examples of tetrahedrally coordinated copper.

Introduction

The preparation of "CuVO₃" was first reported as part of a study of the Cu–V–O system (*1, 2*). Recently (*3*), single crystals of α-copper vanadate (α denotes an ambient pressure phase) have been grown and electrical and magnetic data were reported. As part of a series of papers describing the crystal structures of $CuVO_3$ phases—$CuVO_3(I)$ or $Cu^{2+}V^{4+}O_3$ (*4*) and $CuVO_3(II)$ or $Cu^+V^{5+}O_3$ (*5*)—we now report the structure of α-copper vanadate.

Experimental Methods

Small single crystals of α-copper vanadate, prepared (*3*) by the hydrothermal reaction of Cu_2Cl_2 and $NaVO_3$ in a gold tube, were generously supplied by Professor B. L. Chamberland. An approximately rectangular prismatic crystal was selected; precession photographs confirmed the symmetry to be rhombohedral with possible space groups $R3$ or $R\bar{3}$.

The lattice parameters were determined in a PICK-II least-squares refinement program, using 48 reflections within the angular range

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$35° < |2\theta| < 47°$; the reflections were automatically centered on a Picker FACS-I four-circle diffractometer using $MoK\alpha_1$ radiation. At 22°C the lattice parameters for the triply primitive hexagonal unit cell are $a = 12.857(3)$ and $c = 7.161(2)$ Å; the parameters for the rhombohedral unit cell as $a_R = 7.797(2)$ Å and $\alpha = 111.06(1)°$. The numbers in parentheses represent the standard deviations in the last reported number. These parameters are in excellent agreement with those derived from the refined powder diffraction data (*3*). The calculated density based on the stoichiometry $Cu_{6.78}V_6O_{18.78}$ for the rhombohedral unit cell (*vide infra*) is 5.038 g/cm³ ($V_R = 341.7$ Å³).

Diffraction intensities were measured using Zr-filtered $MoK\alpha$ 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 1.9° with allowance for dispersion and with 40-sec background counts taken at both ends of the scan. Of the 742 independent data investigated in the angular range $2\theta < 62°$, 178 were indiscernible on the recording chart monitor and were discarded as being unobservable, leaving 564 observed data. Three reflections were systematically monitored and no variations in intensities greater than 4% were observed over the entire data collection period. However, since the small changes which did occur could be corre-

lated with daily temperature changes, small corrections were made in the intensities on the basis of a series of linear functions. The maximum correction applied was 2.2%.

The intensity data were also corrected for Lorentz and polarization effects, and absorption corrections were made using a computer program written by N. W. Alcock and modified by B. Lee

A reasonable model which does not require mixed valency (assuming Cu^{2+}) is $Cu_{7-x}V_6O_{19-x}$. With this in mind the refinement of the structure was carried out on two different stoichiometries: in one refinement a vanadium, V(0), was placed at the origin; in the other a copper, Cu(0), was placed at the origin and its occupancy was allowed to vary. The results were as follows:

	using V(0)		using Cu(0)	
isotropic refinement	$R = 0.063$ $R_w = 0.073$	0.060 0.070	0.79(1) occupancy	
anisotropic refinement	$R = 0.053$ $R_w = 0.062$	0.050 0.059	0.78(1) occupancy	

for a crystal of general shape. Input for the program included the indices of the plane faces of the crystal, which were determined 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 54% of $|F_o|$. The uncertainty in the observed structure factor was defined as $\sigma_F = 0.02|F_o| + [C + k^2B]^{1/2}/2|F_o|Lp$, where C is the scan count, k is the ratio of scanning time to the total background count time, and B is the total background count.

All structural refinements (6) mentioned below employed a $1/\sigma^2$ weighting scheme, zerovalent scattering factors for Cu, V, and O (7), and corrections for secondary extinction (8) and anomalous dispersion.

Determination and Refinement of the Structure

Analysis of the Patterson map using the hexagonal unit cell assuming $R\bar{3}$ symmetry unambiguously revealed a copper atom and a vanadium atom, each on a general position. A difference Fourier synthesis using these two atoms indicated three oxygen atoms on general positions, one oxygen atom at the special position $00\frac{1}{2}$ (symmetry $\bar{3}$), and an additional heavy atom at special position 000 (symmetry $\bar{3}$). The intensity of the difference Fourier peak at the origin indicated a vanadium, making the stoichiometry $Cu_6V_7O_{19}$, which can be charge-balanced only by assuming mixed valency at one or both of the metal atoms. The hydrothermal preparation, however, does not suggest mixed valency.

For the Cu(0) refinement the figure of merit decreased to 1.341 from its value of 1.416 for the V(0) refinement.

It was immediately noticed that the partial occupancy of 78% for Cu(0) corresponds approximately to full vanadium occupancy ($0.78 \times 29 = 22.6$; $V = 23$). Furthermore, the bond length from the atom in question to its six surrounding oxygens is 2.02 Å, which would be expected for six-coordinated V^{3+} (9). One could argue on this basis that there actually is a vanadium at the origin and that the lower R using Cu(0) is within the (indeterminate) error of the scattering factors used, or is due to truncation errors.

Two additional anisotropic refinements were carried out, one using Cu(0) and the other V(0), in which occupancies of all atoms were allowed to vary (holding the scale factor constant). In neither refinement did any oxygen occupancy decrease. However, if a deficiency of 0.22 oxygen atoms [matching the deficiency in Cu(0)] were spread over 19 atoms, the result would be undetectable within the error (~2%) of the occupancy factors. Hence Cu(0) cannot be ruled out on the basis of apparent full oxygen occupancy.

In the anisotropic refinement using V(0), the V(0) occupancy rose to 113%, whereas the occupancies of the two metals on general positions remained at 100%. It is apparent from this and from the lower R using Cu(0) that the electron density at the origin is better described by the scattering factor for copper. For this reason and because a nonmixed valency model seems to be indicated, we propose the stoichiometry $Cu_{6.78}V_6O_{18.78}$ for the crystal of α-copper vanadate examined.

TABLE I

Observed and Calculated Structure Factors

H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOUS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FODS	FCAL
-9	15	6	335	283	-5	9	4	837	824	-4	15	-1	570	579	-2	4	6	738	677	-1	3	2	1766	1730
-9	17	4	1458	1392	-5	9	7	444	457	-4	15	2	489	431	-2	4	9	648	658	-1	3	5	256	178
-8	11	8	442	478	-5	10	6	278	203	-4	15	5	463	376	-2	5	2	479	452	-1	3	8	652	647
-8	12	7	304	252	-5	11	2	1198	1189	-4	16	1	534	560	-2	5	5	572	491	-1	4	1	4981	5096
-8	13	6	1026	1028	-5	11	5	566	600	-4	16	4	213	19	-2	6	1	1566	1494	-1	4	4	477	445
-8	14	5	462	435	-5	11	8	408	376	-4	17	-3	372	338	-2	6	4	602	583	-1	4	7	209	238
-8	15	4	458	469	-5	12	1	2812	2686	-4	17	3	678	653	-2	6	7	1838	1807	-1	4	10	1276	1338
-8	16	3	926	831	-5	12	4	211	98	-3	5	4	6715	6710	-2	7	3	175	164	-1	5	0	2930	2781
-8	17	2	1025	1007	-5	12	7	523	483	-3	5	10	741	776	-2	7	6	2304	2279	-1	5	3	508	509
-8	18	1	574	520	-5	13	0	395	398	-3	6	3	602	543	-2	7	9	915	984	-1	5	6	729	644
-7	1C	7	570	576	-5	13	3	679	626	-3	6	6	228	229	-2	8	-1	565	575	-1	5	9	479	586
-7	11	6	1306	1317	-5	14	-1	565	593	-3	6	9	564	475	-2	8	5	1058	1059	-1	6	-1	917	916
-7	13	4	226	252	-5	14	2	1311	1230	-3	7	2	1294	1291	-2	8	8	295	310	-1	6	2	1239	1262
-7	14	6	1528	1498	-5	14	5	374	449	-3	7	5	543	493	-2	9	-2	654	668	-1	6	5	501	398
-7	15	-5	502	461	-5	15	-2	780	744	-3	7	8	1006	1014	-2	9	1	1057	1021	-1	6	8	306	253
-7	16	1	390	228	-5	15	1	216	248	-3	8	1	931	912	-2	9	4	226	215	-1	7	-2	839	859
-7	16	4	412	409	-5	16	-3	38C	327	-3	8	4	435	405	-2	9	7	445	466	-1	7	4	562	558
-7	17	0	205	92	-5	16	0	375	320	-3	9	0	353	291	-2	10	-3	824	812	-1	7	7	321	254
-7	17	3	379	338	-5	17	2	1025	974	-3	9	3	2161	2155	-2	10	0	430	406	-1	8	0	6896	6583
-7	18	-1	549	571	-5	18	1	583	525	-3	9	6	324	324	-2	10	3	1291	1317	-1	8	3	391	349
-6	7	8	467	373	-4	5	6	415	366	-3	10	-1	382	374	-2	10	6	1124	1130	-1	8	6	735	687
-6	8	7	762	714	-4	5	9	659	644	-3	10	2	1006	1011	-2	11	-4	621	597	-1	9	-1	1285	1351
-6	10	5	1586	1559	-4	7	7	352	419	-3	10	5	481	459	-2	11	2	576	545	-1	9	-4	244	227
-6	1C	8	1994	2C41	-4	8	6	541	554	-3	11	-2	2819	2733	-2	11	5	365	290	-1	9	-1	494	461
-6	11	4	766	789	-4	8	9	253	252	-3	11	4	948	958	-2	11	8	385	380	-1	9	2	520	516
-6	11	7	281	280	-4	9	2	2803	2732	-3	11	7	2245	2270	-2	12	-2	1110	1102	-1	9	5	493	508
-6	12	6	319	256	-4	9	5	2159	2155	-3	12	0	712	679	-2	12	1	2351	2313	-1	9	8	326	264
-6	13	2	677	605	-4	10	1	582	550	-3	12	3	512	472	-2	12	4	311	309	-1	10	-5	816	857
-6	13	5	387	342	-4	10	4	1535	1553	-3	12	6	418	349	-2	12	7	263	257	-1	10	-2	914	927
-6	14	1	797	777	-4	10	7	155	246	-3	13	-4	939	889	-2	13	-3	381	340	-1	10	4	1590	1629
-6	14	4	365	366	-4	11	3	1013	981	-3	13	2	206	265	-2	13	0	2017	1941	-1	10	7	370	346
-6	15	0	524	490	-4	11	6	408	382	-3	13	5	428	462	-2	13	3	288	179	-1	11	-3	863	880
-6	15	3	263	249	-4	12	-1	779	747	-3	14	-1	903	882	-2	14	-1	679	606	-1	11	3	333	323
-6	15	6	275	310	-4	12	2	497	495	-3	14	1	820	765	-2	14	2	493	450	-1	11	6	474	483
-6	16	-1	2394	2349	-4	13	-2	306	250	-3	15	-3	2030	1970	-2	15	-5	444	430	-1	12	-1	1536	1482
-6	16	2	1606	1582	-4	13	1	1028	966	-3	15	0	231	209	-2	15	-2	451	641	-1	12	2	540	525
-6	16	5	218	182	-4	13	4	2636	2671	-3	15	3	416	455	-2	16	-3	354	349	-1	13	-2	718	694
-6	17	-2	225	256	-4	13	7	233	158	-3	16	-1	248	292	-2	16	0	1863	1821	-1	14	-3	472	428
-6	18	0	558	572	-4	14	-3	290	288	-3	17	-2	657	619	-2	16	3	340	358	-1	14	0	465	481
-5	6	7	1554	1475	-4	14	0	442	372	-3	17	1	949	918	-2	17	-1	430	416	-1	14	3	2358	2409
-5	7	6	632	632	-4	14	3	511	530	-2	3	4	979	953	-1	2	3	1165	1067	-1	15	-4	286	273
-5	7	9	490	535	-4	14	6	193	34	-2	3	7	2908	2834	-1	2	6	2667	2512	-1	15	-1	352	297
-5	8	8	995	1010	-4	15	-4	1206	1108	-2	3	10	397	320	-1	2	9	712	618					

H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL
-1	16	1	302	321	0	12	-3	1075	1122	1	8	5	1028	1012	2	6	5	535	463	3	4	5	1026	1056
0	0	3	551	359	0	12	3	586	605	1	8	8	774	799	2	6	8	235	214	3	4	8	518	611
0	0	6	1363	1258	0	12	6	1094	1122	1	9	-2	763	793	2	7	-5	1594	1651	3	5	-2	2281	2476
0	0	9	1779	1710	0	13	-4	472	439	1	9	7	602	632	2	7	-2	1899	2005	3	5	1	4766	4760
0	1	5	1237	1126	0	13	-1	1189	1148	1	10	-6	675	661	2	7	1	479	445	3	5	7	659	654
0	1	8	673	605	0	13	2	798	755	1	10	-3	417	430	2	7	4	575	556	3	6	-3	837	870
0	2	1	437	503	0	14	-2	3C0	193	1	10	0	468	416	2	7	7	1655	1736	3	6	0	694	7C4
0	2	4	1970	1805	0	14	4	613	571	1	10	3	346	350	2	8	-6	660	680	3	6	6	635	664
0	2	1C	368	271	0	15	-3	1248	1244	1	10	6	333	305	2	8	0	400	327	3	6	9	542	602
0	3	0	988	1018	0	16	-1	580	612	1	11	-4	2564	2677	2	8	3	631	627	3	7	-4	364	340
0	3	3	331	226	1	0	4	745	679	1	11	-1	981	970	2	8	6	357	352	3	7	-1	1201	1246
0	3	6	534	930	1	0	7	544	478	1	11	2	222	243	2	9	-7	595	574	3	7	2	1121	1105
0	4	-1	3996	4223	1	0	10	443	623	1	11	5	1189	1189	2	9	-1	3393	3401	3	7	5	369	348
0	4	2	2392	2316	1	1	0	514	487	1	12	-2	949	942	2	9	2	1836	1865	3	8	-5	736	770
0	4	5	585	542	1	1	3	4561	4243	1	12	1	383	363	2	9	8	405	853	3	8	-2	810	871
0	4	8	768	803	1	1	6	945	887	1	13	0	1186	1197	2	10	-5	234	287	3	8	1	864	861
0	5	-2	1525	1630	1	2	-1	388	455	1	14	-1	298	292	2	10	4	821	816	3	8	7	503	468
0	5	1	681	623	1	2	2	4616	4236	1	15	-2	475	447	2	10	7	368	310	3	9	-3	260	202
0	5	4	659	600	1	2	5	2869	2798	2	0	2	1826	1892	2	11	0	779	773	3	9	0	1414	1431
0	5	7	573	587	1	3	-2	41C	408	2	0	5	1012	956	2	11	3	397	363	3	9	6	171	127
0	6	-3	276	292	1	3	1	1745	1761	2	0	8	487	350	2	12	-4	268	269	3	10	-7	1156	1119
0	6	0	263	199	1	3	4	1C55	1058	2	1	1	593	624	2	12	2	758	785	3	10	-1	503	455
0	6	3	4835	4661	1	3	10	512	530	2	1	4	946	888	2	12	5	715	700	3	10	2	1138	1160
0	6	6	1103	1059	1	4	-3	976	1006	2	1	7	716	681	2	13	-5	223	224	3	10	5	939	920
0	6	9	261	203	1	4	0	1041	1043	2	2	0	1690	1734	2	13	-2	1285	1344	3	11	-5	783	773
0	7	-4	689	720	1	4	3	1512	1443	2	2	3	847	784	2	13	1	2109	2148	3	11	-2	366	325
0	7	-1	438	426	1	4	6	1198	1226	2	2	6	3C7	336	2	14	-3	322	389	3	11	1	750	814
0	7	2	421	432	1	5	-4	834	816	2	3	-1	793	1002	2	15	-1	366	389	3	11	4	1460	1495
0	7	5	562	560	1	5	-1	1804	1833	2	3	2	2137	1932	3	0	3	1183	1220	3	12	3	536	531
0	7	8	660	690	1	5	2	2796	2748	2	3	5	2089	2010	3	0	6	737	708	3	13	-1	332	313
0	8	-5	418	365	1	5	5	1163	1049	2	3	8	2772	2891	3	0	9	374	324	3	13	2	484	523
0	8	1	369	330	1	6	-5	546	454	2	4	-2	1553	1598	3	1	2	2505	2732	3	14	1	594	573
0	8	4	655	613	1	6	-2	940	996	2	4	1	1467	1429	3	1	5	501	482	4	0	4	338	229
0	9	-6	1204	1217	1	6	4	1446	1418	2	4	4	859	814	3	1	8	823	843	4	0	10	1229	1183
0	9	-3	948	985	1	7	-6	654	628	2	4	7	541	588	3	2	1	712	786	4	1	6	561	617
0	9	3	1226	1206	1	7	-3	2936	3090	2	5	-3	530	539	3	2	10	329	369	4	1	9	467	517
0	9	6	534	574	1	7	0	255	181	2	5	0	1927	1958	3	3	0	1420	1375	4	2	2	2663	3044
0	10	-7	2053	2040	1	7	3	339	345	2	5	3	218	133	3	3	3	840	814	4	2	5	1328	136C
0	10	-4	749	765	1	7	6	1831	1795	2	5	6	699	699	3	3	6	1020	1032	4	2	8	331	302
0	10	2	2326	2343	1	7	9	6C0	603	2	5	9	326	163	3	3	9	408	401	4	3	1	831	873
0	1C	5	2015	2053	1	8	-4	1963	2014	2	6	-4	236	216	3	4	-4	1385	1607	4	3	4	1700	1713
0	11	1	913	915	1	8	-1	459	465	2	6	-1	484	564	3	4	2	2183	2071	4	3	7	296	325
0	11	4	378	341	1	8	2	782	813	2	6	2	1042	1048						4	4	0	866	864

H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL	H	K	L	FOBS	FCAL
4	4	3	794	823	5	1	4	647	599	5	11	-3	351	294	6	9	3	518	461	8	5	3	701	709
4	4	6	561	592	5	2	3	4067	4264	5	11	1	817	777	6	10	-1	838	866	8	5	6	648	630
4	5	-1	557	629	5	2	6	851	839	5	13	1	746	757	6	10	2	620	601	8	6	2	669	695
4	5	2	527	493	5	3	2	922	975	6	0	6	2629	2619	6	11	-2	336	477	8	6	5	487	504
4	5	5	239	123	5	3	5	438	464	6	0	9	1072	1090	7	0	7	353	69	8	7	1	385	422
4	6	-2	588	629	5	4	1	321	289	6	1	5	902	923	7	1	6	716	693	8	7	4	1199	1243
4	6	1	1127	1101	5	4	4	576	611	6	1	8	506	507	7	1	9	1303	1349	8	8	0	225	272
4	6	4	4067	4034	5	4	7	2166	2282	6	2	4	306	484	7	2	5	779	834	8	9	-1	414	520
4	6	7	3C4	163	5	5	0	1264	1287	6	2	7	460	457	7	3	4	679	740	8	9	2	295	270
4	7	-3	689	721	5	5	3	233	265	6	3	3	781	772	7	3	7	390	386	8	10	-2	352	333
4	7	0	334	332	5	6	-1	386	372	6	3	6	1319	1392	7	4	3	311	273	8	10	1	267	270
4	7	3	1194	1169	5	6	2	748	759	6	3	9	461	423	7	4	6	479	496	9	1	8	625	630
4	8	-4	835	845	5	6	5	332	370	6	4	2	597	645	7	5	2	1252	1298	9	2	7	471	471
4	8	-1	370	292	5	7	-2	1361	1440	6	4	5	674	712	7	6	1	332	323	9	4	5	1118	1187
4	8	2	833	846	5	7	1	1435	1435	6	4	8	837	883	7	7	7	482	425	9	6	3	332	282
4	9	-2	325	271	5	7	4	373	403	6	5	1	1548	1557	7	7	3	2389	2462	9	6	6	414	416
4	9	1	899	915	5	7	7	459	453	6	5	4	405	460	7	7	6	610	603	9	7	2	249	280
4	10	-6	986	980	5	8	-3	2854	3000	6	6	0	2232	2212	7	8	-1	352	388	9	7	5	457	457
4	10	3	1679	1684	5	8	0	582	495	6	6	3	193	82	7	8	2	281	211	9	8	1	201	131
4	11	-1	319	316	5	8	3	525	532	6	6	6	260	312	7	10	-3	797	831	9	8	4	247	249
4	11	2	463	389	5	9	2	1849	1931	6	7	-1	272	281	7	11	2	1508	1571	10	3	7	206	66
4	12	-2	1586	1570	5	9	5	481	476	6	7	2	609	600	8	0	8	624	659	10	4	6	698	723
4	12	4	568	589	5	10	-5	938	555	6	8	-2	547	556	8	1	7	394	382	10	5	5	817	821
4	13	-3	349	354	5	10	-2	411	389	6	8	1	278	280	8	2	6	474	487	10	6	6	291	309
4	13	0	459	490	5	10	1	715	772	6	9	-3	202	330	8	3	3	2130	2271	10	7	3	264	264
5	C	8	516	463	5	10	4	245	192	6	9	0	2546	2612	8	4	4	328	363	10	8	2	405	429
																				8	4	7	375	382					

TABLE II

FRACTIONAL HEXAGONAL ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS[a]

	Position	$10^4 x$	$10^4 y$	$10^4 z$	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(0)*	3(a)	0	0	0	0.64(7)	B_{11}	0.48(9)	$\frac{1}{2}B_{11}$	0	0
Cu(1)	18(f)	4295.3(8)	549.2(8)	2363(1)	1.35(4)	0.95(4)	1.40(4)	0.46(3)	0.06(3)	0.00(3)
V	18(f)	1530(1)	176(1)	3282(2)	0.70(4)	0.91(4)	0.67(4)	0.47(3)	0.48(3)	0.02(3)
O(1)	18(f)	2634(4)	337(4)	1870(8)	0.99(18)	1.10(17)	0.89(18)	0.58(15)	0.01(14)	0.03(14)
O(2)	18(f)	8761(5)	9830(4)	1898(7)	1.21(18)	1.03(18)	1.13(19)	0.87(16)	−0.32(15)	−0.27(14)
O(3)	18(f)	8525(4)	895(4)	4972(7)	0.72(16)	0.81(16)	0.78(17)	0.38(14)	0.15(14)	0.15(14)
O(4)	3(b)	0	0	$\frac{1}{2}$	0.80(25)	B_{11}	0.96(44)	$\frac{1}{2}B_{11}$	0	0

* Occupancy factor = 0.78(1) (see text).

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. The B's are defined by the general temperature factor $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

The final anisotropic refinement, in which the occupancy of Cu(0) only was allowed to vary, yielded a residual $R = 0.050$ and $R_w = 0.059$. There were 564 data and 52 independently varied parameters for a data to parameter ratio of 10.8. The maximum secondary extinction correction was 2.2% of $|F_c|$ for the $\bar{1}80$ reflection. The calculated and observed structure factors are listed in Table I. The atomic positions and the anisotropic temperature factors are listed in Table II.

Discussion

The structure of $Cu_{6.78}V_6O_{18.78}$ (α-copper vanadate) is based on a cubic close-packed array of oxygen ions, the stacking direction being the hexagonal c axis. There are three oxygen layers in the hexagonal unit cell, each ideally consisting of 19 oxygens. The vanadium and Cu(0) ions occupy distorted octahedral sites, while Cu(1) ions occupy distorted tetrahedral sites.

The vanadium octahedra are arranged in groups of six about the oxygen at the special position $00\frac{1}{2}$. Each octahedron shares edges with four other octahedra in the group, two at the same z-level and two in the adjacent level. These groups of vanadium octahedra are linked in chains along the threefold axis through edge-sharing with the Cu(0) octahedron at the other $\bar{3}$ position on the axis. The upper three edges of this octahedron are shared by three vanadium octahedra of the group above, and the lower three edges by three vanadium octahedra of the group below. Two of these parallel chains are shown in Fig. 1, a stereoscopic view of the structure as seen along the a axis.

The vanadium and copper octahedra about one threefold axis are linked to octahedra about other threefold axes through corner-sharing with
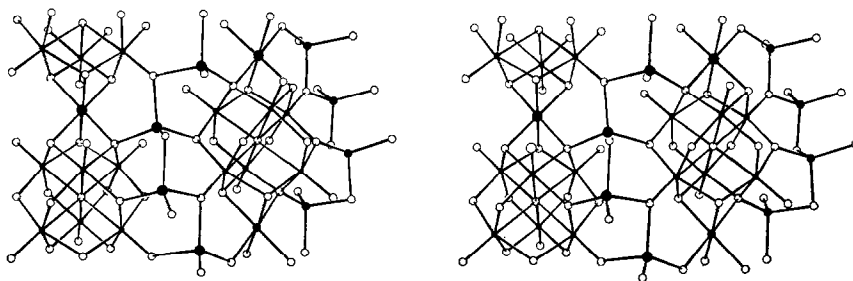
FIG. 1. Stereoscopic view of the α-copper vanadate structure as seen in the x direction; z is towards the top of the page. (O) oxygen, (●) vanadium, and (⬤) copper. Groups of six vanadium octahedra may be seen at the lower left and to the right of the center. An octahedral copper, Cu(0), is seen above the group at left linking it to another group of vanadium octahedra above. Two spiral chains of Cu(1) tetrahedra may also be seen: one just to the left of center in which tetrahedra point upward, and one at the far right in which the tetrahedra point downward.

O • 1/6
Cu(1) ▲ 3/12
Cu(0) ● 0
Cu(1) ▽ 1/12
V ○ 0

O • 1/2
Cu(1) ▲ 7/12
Cu(1) ▽ 5/12
Cu(0) ● 1/3
V ○ 1/3

O • 5/6
Cu(0) ● 2/3
Cu(1) ▲ 11/12
Cu(1) ▽ 9/12
V ○ 2/3
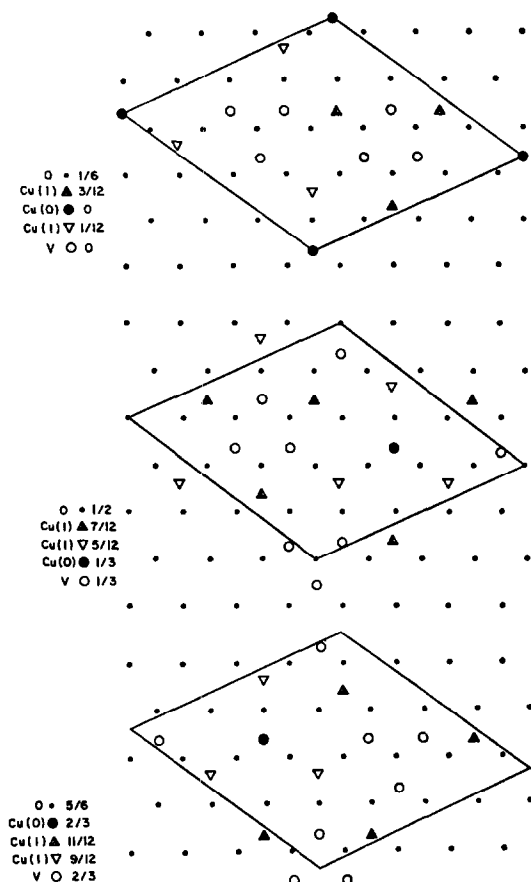
FIG. 2. Idealized layer by layer representation of the α-copper vanadate structure as viewed down the c-axis. The numbers in the legend are heights in fractional units of c. (△) Cu(1) tetrahedra which point downward; (▲) Cu(1) tetrahedra which point upward.

copper tetrahedra. The copper atoms are very close to, but not on, the threefold screw axis, so that the copper tetrahedra occur in corner-linked spiral chains parallel to the axis. These corner linkages can also be seen in Fig. 1.

A layer by layer diagram of the idealized structure is shown in Fig. 2, and bond distances, angles, and polyhedral edge lengths are given in Tables III and IV.

The structural evidence supports the valence distribution Cu^{2+}, V^{4+}. If the oxygen bound to six vanadium atoms, O(4), is examined in the light of Pauling's electrostatic valence rules (10) assuming V^{4+} and Cu^{2+}, a charge of -4 (an excess negative charge of 2) is found to reside here. To our knowledge this excess is larger than for any oxygen in any other compound (11). Although the anomalously long V–O(4) bond

compensates for this excess charge at O(4), vanadium as V^{5+} would render the situation intolerable. Furthermore, the assignment of a $+5$ oxidation state to the vanadium would leave univalent copper in a fully occupied tetrahedral site, which would be highly unlikely.

One might also consider the vanadium as V^{3+} if it is recognized that hydrogen could be incorporated into the structure on a general position as the result of the hydrothermal preparation. A complete difference Fourier synthesis, however, showed no areas of residual electron density corresponding to more than 0.2 electrons. Furthermore, the bond distances clearly indicate a higher oxidation state, as follows: The average V–O bond distance is 1.933 Å, which gives an ionic radius of 0.55 Å when 1.38 Å is subtracted for the oxygen radius. Shannon and Prewitt (9) give ionic radii for the six-coordinated ions as follows: V^{3+}, 0.64; V^{4+}, 0.59; V^{5+}, 0.54 Å. Hence the vanadium in this structure is obviously V^{4+} or V^{5+}, and V^{5+} has been ruled out. The final formulation, then, is $Cu_{6.78}V_6^{4+}O_{18.78}$.

Divalent copper ion is usually found in a distorted octahedral, square planar, square pyramidal or triangular bipyramidal coordination. α-Copper vanadate is one of the few examples of Cu^{2+} in a tetrahedral coordination. The spinels $CuCr_2O_4$ (12) and $CuCo_2O_4$ (13) have been shown to contain tetrahedral Cu^{2+} as does the halide Cs_2CuCl_4 (14). Our calculation of the average tetrahedral Cu–O bond distance in $CuCr_2O_4$ (1.94 Å) is in good agreement with the average value for Cu(1)–O in α-copper vanadate (2.003 Å).

The structures of a series of copper–vanadium bronzes—β-$Cu_xV_2O_5$, $0.26 \leqslant x \leqslant 0.64$ (15); ε-$Cu_xV_2O_5$, $0.67 \leqslant x \leqslant 0.86$ (15); $Cu_xV_4O_{11}$, $x = 1.82$ (16)—have been determined and are based on $(V_2O_5)_n$ or $(V_4O_{11})_n$ networks with the copper atoms located in partially occupied highly distorted four-, five-, and six-coordinated sites between the layers. An analysis (17) of their electrical and magnetic properties concludes that the copper is present in the $+1$ state in the $Cu_xV_2O_5$ compounds and as a mixture of Cu^+ and Cu^{2+} in $Cu_xV_4O_{11}$ (16). It should be noted that there is no structural relationship between these vanadium bronzes and α-copper vanadate.

α-Copper vanadate was originally formulated as "$CuVO_3$" with a region of nonstoichiometry corresponding to the formula $CuVO_{3-x}$ ($x \leqslant 0.20$) (2). Unfortunately, the supporting experimental details for this formulation are sketchy,

TABLE III

BOND DISTANCES, BOND ANGLES, AND POLYHEDRAL EDGE LENGTHS FOR METAL POLYHEDRA[a]

	Distance (Å)	Angle (°)	Edge length (Å)
i. Cu(0) polyhedron[b]			
3 × Cu(0)–O(2)	2.021(5)		
3 × Cu(0)–O(2′)	2.021(5)		
3 × O(2)–Cu(0)–O(2)		79.7(2)	2.590(8)
3 × O(2′)–Cu(0)–O(2′)		79.7(2)	2.590(8)
6 × O(2)–Cu(0)–O(2′)		100.3(2)	3.10(1)
3 × O(2)–Cu(0)–O(2′)		180	
ii. Cu(1) polyhedron[b]			
Cu(1)–O(1′)	2.039(6)		
Cu(1)–O(1)	2.044(5)		
Cu(1)–O(2)	1.966(5)		
Cu(1)–O(3)	1.962(5)		
O(1′)–Cu(1)–O(1)		100.5(2)	3.139(5)
O(1′)–Cu(1)–O(2)		105.4(2)	3.186(8)
O(1′)–Cu(1)–O(3)		108.3(2)	3.243(8)
O(1)–Cu(1)–O(2)		112.4(2)	3.333(7)
O(1)–Cu(1)–O(3)		107.5(2)	3.230(7)
O(2)–Cu(1)–O(3)		120.8(2)	3.416(7)
iii. V polyhedron[c]			
V–O(1)	1.670(5)		
V–O(2)	1.950(5)		
V–O(2′)	2.003(5)		
V–O(3)	1.836(5)		
V–O(3′)	1.902(5)		
V–O(4)	2.234(1)		
O(1)–V–O(2)		98.7(2)	2.753(7)
O(1)–V–O(2′)		98.0(2)	2.780(7)
O(1)–V–O(3)		102.6(2)	2.737(7)
O(1)–V–O(3′)		101.7(2)	2.774(7)
O(2)–V–O(2′)		81.9(3)	2.590(8)
O(2)–V–O(3)		92.8(2)	2.742(7)
O(2)–V–O(4)		79.3(2)	2.678(5)
O(2′)–V–O(3′)		87.0(2)	2.688(7)
O(2′)–V–O(4)		78.2(1)	2.678(5)
O(3)–V–O(3′)		91.0(1)	2.666(5)
O(3)–V–O(4)		81.2(1)	2.666(5)
O(3′)–V–O(4)		79.8(1)	2.666(5)
O(1)–V–O(4)		175.9(3)	
O(2)–V–O(3′)		157.9(2)	
O(2′)–V–O(3)		159.3(2)	

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

[b] The primed and unprimed oxygens occur in different close-packed layers of the structure.

[c] The primed and unprimed oxygens are in the same layer and symmetry related.

TABLE IV

BOND DISTANCES, BOND ANGLES, AND POLYHEDRAL EDGE LENGTHS FOR OXYGEN POLYHEDRA[a]

	Distance (Å)	Angle (°)	Edge length (Å)
i. O(1) polyhedron			
O(1)–V	1.670(5)		
O(1)–Cu(1)	2.039(6)		
O(1)–Cu(1')	2.040(6)		
V–O(1)–Cu(1)		132.7(3)	3.405(2)
V–O(1)–Cu(1')		131.6(3)	3.387(2)
Cu(1)–O(1)–Cu(1')		95.7(2)	3.027(1)
ii. O(2) polyhedron[b]			
O(2)–Cu(0)	2.021(5)		
O(2)–Cu(1)	1.966(5)		
O(2)–V	1.950(5)		
O(2)–V'	2.003(5)		
Cu(0)–O(2)–Cu(1)		118.0(3)	3.417(1)
Cu(0)–O(2)–V		98.1(2)	3.000(1)
Cu(0)–O(2)–V'		96.4(2)	3.000(1)
Cu(1)–O(2)–V		114.3(3)	3.291(2)
Cu(1)–O(2)–V'		117.6(2)	3.395(2)
V–O(2)–V'		109.6(2)	3.230(2)
iii. O(3) polyhedron[c]			
O(3)–Cu(1)	1.962(5)		
O(3)–V	1.836(5)		
O(3)–V'	1.902(5)		
Cu(1)–O(3)–V		121.1(2)	3.308(2)
Cu(1)–O(3)–V'		122.4(3)	3.385(2)
V–O(3)–V'		111.4(2)	3.088(2)
iv. O(4) polyhedron[c]			
3 × O(4)–V	2.234(1)		
3 × O(4)–V'	2.234(1)		
3 × V–O(4)–V		92.58(4)	3.230(2)
3 × V'–O(4)–V'		92.58(4)	3.230(2)
6 × V–O(4)–V'		87.42(4)	3.088(2)
3 × V–O(4)–V'		180	

[a] Numbers in parentheses are estimated standard deviations in the last figure.
[b] The primed and unprimed vanadiums are in the same layer and symmetry related.
[c] The primed and unprimed vanadiums are symmetry related and in different layers.

the only details being the conditions of preparation of the nonstoichiometric phases (heating in vacuum) and some powder X-ray diffraction patterns. We were able to index these admittedly poor patterns on the basis of our reported hexagonal unit cell for α-copper vanadate. There is a definite trend in the c/a ratio which decreases from 0.577 to 0.546 with increasing x for the formula $CuVO_{3-x}$. Realizing that powder X-ray diffraction has a sensitivity limitation of ~5% it is possible that this reported oxygen deficiency could actually be an exsolution of a copper oxide which would be difficult to detect at this level. Of course, the nonstoichiometry reported by Raveau, could be the result of oxygen loss but, due to the lack of experimental details, no definite

conclusion can be reached. However, realizing the nature of the chains of linked octahedra in the structure, the loss of copper as a copper oxide from the Cu(0) position would favor a decrease in the c/a ratio.

Acknowledgment

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