

The Crystal Structure of $\text{CuVO}_3(\text{I})$, a Distorted Ilmenite-Type Derivative

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The crystal structure of a high-pressure phase, $\text{CuVO}_3(\text{I})$, has been determined and refined by full-matrix least-squares procedures using automatic diffractometer data to a residual $R = 0.055$ ($R_w = 0.070$). The space group is triclinic, PI , with $a = 4.9646(10)$, $b = 5.4023(7)$, $c = 4.9154(7)$ Å, $\alpha = 90.32(1)$, $\beta = 119.13(1)$, and $\gamma = 63.93(1)^\circ$; $Z = 2$. This structure is the first example of a triclinic distortion of the ilmenite structure-type and is discussed in terms of its crystal chemistry. Analysis of interatomic distances indicates the valence distribution to be $\text{Cu}^{2+}\text{V}^{4+}\text{O}_3$. The anomalous paramagnetic moment is discussed in terms of $\text{V}^{4+}\text{-V}^{4+}$ interactions.

Introduction

Recently, the compounds CuVO_3 (1), CoVO_3 (1), NiVO_3 (2) and MnVO_3 (3) have been found to form at high pressures as triclinic phases which, on the basis of a strong similarity of their powder X-ray diffraction patterns, were thought to be related to the rhombohedral ilmenite structure-type. We have completed a single crystal X-ray structural investigation of one of these compounds, $\text{CuVO}_3(\text{I})$ [the symbol (I) indicates the high-pressure phase following the notation of Ref. (1) and (4)], and herein report its crystal structure as being the first example of a triclinic distortion of the ilmenite structure type.

Experimental

Small single crystals of $\text{CuVO}_3(\text{I})$ were generously supplied by Professor B. L. Chamberland. Their preparation at 65 kbar and 600–1000°C has been described (1). An irregularly shaped crystal was selected; Weissenberg and precession photographs confirmed the symmetry to be triclinic.

The lattice parameters were determined in a PICK II least-squares refinement program, using 48 reflections within the angular range $39^\circ < 2\theta < 53^\circ$; the reflections were automatically centered

on a Picker FACS-I four circle diffractometer using $\text{MoK}\alpha_1$ radiation. At 22°C the lattice parameters are $a = 4.9646(10)$, $b = 5.4023(7)$, $c = 4.9154(7)$ Å, $\alpha = 90.32(1)$, $\beta = 119.13(1)$, and $\gamma = 63.93(1)^\circ$, where the figures in parentheses represent the standard deviations in the last reported figure. These parameters are in excellent agreement with those derived from the refined powder diffraction data (1). The calculated density, with $Z = 2$, is 5.409 g/cm³.

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 903 independent data investigated in the angular range $2\theta < 71^\circ$, a total of 881 were considered observable according to the criterion $|F_o| > 0.675\sigma_F$, where σ_F is defined as $0.02|F_o| + [C + k^2 B]^{1/2}|F_o|/Lp$; the total scan count is C , and 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.

The intensity data were corrected for Lorentz and polarization effects, and absorption corrections were made. Since the crystal was irregularly

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TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS

M	K	L	F0BS	FCAL	M	K	L	F0BS	FCAL	M	K	L	F0BS	FCAL	M	K	L	F0BS	FCAL	M	K	L	F0BS	FCAL	M	K	L	F0BS	FCAL							
0	0	0	-5	77	75	0	3	6	57	56	1	-6	-1	26	27	1	-2	2	205	208	1	1	5	212	218	1	5	-1	384	375	2	-4	-5	9	10	
0	0	0	-4	364	355	0	4	-4	86	78	1	-6	0	153	179	1	-2	2	407	404	1	1	5	219	217	1	5	0	187	183	2	-4	-4	96	103	
0	0	0	-3	25	11	0	4	-3	115	110	1	-6	1	53	59	1	-2	3	46	43	1	2	-5	214	217	1	5	2	124	117	1	5	0	9	8	25
0	0	0	-2	132	119	0	4	-2	37	37	1	-5	-2	45	45	1	-2	4	43	40	1	2	-4	216	214	1	5	2	38	32	2	-4	-2	378	379	
0	0	0	-1	84	70	0	4	-1	17	7	1	-5	-5	42	40	1	-2	5	41	35	1	2	-4	218	225	1	5	3	373	391	2	-4	-1	89	92	
0	0	0	0	103	108	0	4	0	78	68	1	-5	-4	34	15	1	-1	-7	47	43	1	2	-3	219	223	1	5	4	76	78	2	-4	0	181	180	
0	0	0	0	126	124	0	4	1	41	42	1	-5	-2	37	37	1	-1	-5	348	301	1	2	-1	48	41	1	5	6	20	13	2	-4	2	120	121	
0	0	0	0	14	78	91	0	4	3	39	1	-5	-1	107	106	1	-1	-4	28	22	1	2	0	633	608	1	6	-3	49	46	2	-3	-7	163	137	
0	0	0	0	104	184	0	4	4	224	226	1	-5	0	22	9	1	-1	-3	85	101	1	2	1	121	128	1	6	-2	146	139	2	-3	-6	30	30	
0	0	0	0	131	105	0	4	5	14	11	1	-5	1	242	239	1	-1	-2	164	161	1	2	2	113	118	1	6	-1	177	173	2	-3	-2	65	58	
0	0	0	0	160	137	0	4	6	44	44	1	-5	2	144	139	1	-1	-1	129	109	1	2	3	28	28	1	6	0	111	109	2	-3	-4	71	70	
0	0	0	0	73	62	0	5	-4	3	30	1	-5	3	144	146	1	-1	0	49	40	1	2	4	372	351	1	6	1	86	93	2	-3	-3	409	420	
0	0	0	0	232	252	0	5	-3	233	221	1	-4	-7	58	61	1	-1	-1	461	444	1	2	5	57	64	1	6	2	318	323	2	-3	-2	60	62	
0	0	0	0	105	93	0	5	-2	23	12	1	-4	-6	108	115	1	-1	-2	45	74	1	3	2	173	177	1	6	3	16	22	2	-3	2	167	178	
0	0	0	0	262	250	0	5	-1	117	116	1	-4	-5	37	39	1	-1	-3	277	278	1	3	-6	25	17	1	6	4	54	53	2	-3	0	20	20	
0	0	0	0	35	47	0	5	0	114	114	1	-4	-4	291	320	1	-1	-5	190	109	1	3	-5	100	95	1	6	5	9	8	2	-3	1	328	326	
0	0	0	0	16	21	0	5	1	367	364	1	-4	-3	103	100	1	-1	-4	157	218	1	3	-4	161	168	1	6	2	318	323	2	-3	-2	60	62	
0	0	0	0	23	23	0	5	2	44	44	1	-4	-2	54	73	1	0	-7	7	7	1	0	-3	413	363	1	7	0	29	29	2	-3	3	53	57	
0	0	0	0	21	9	0	5	3	50	46	1	-4	-1	19	15	1	0	-6	281	266	1	3	-2	88	78	1	7	1	154	154	2	-2	-7	19	12	
0	0	0	0	25	27	0	5	4	57	55	1	-4	0	381	368	1	0	-5	19	15	1	3	-1	373	368	1	7	2	145	144	2	-2	-6	236	222	
0	0	0	0	298	286	0	5	5	225	230	1	-4	1	30	29	1	0	-4	114	105	1	3	0	135	129	1	7	3	62	66	2	-2	-5	57	53	
0	0	0	0	105	93	0	5	-1	117	116	1	-4	0	294	287	1	0	-3	67	53	1	3	2	562	579	1	7	4	43	45	2	-2	-4	326	346	
0	0	0	0	35	47	0	5	0	114	114	1	-4	-4	164	168	1	0	-2	611	608	1	3	2	43	35	1	8	0	85	82	2	-2	-3	62	60	
0	0	0	0	136	126	0	6	-2	169	153	1	-3	-7	203	194	1	0	-1	53	40	1	3	3	337	334	1	8	1	167	168	2	-2	-2	284	284	
0	0	0	0	192	210	0	6	-1	49	44	1	-3	-6	26	27	1	0	0	214	223	1	3	4	231	216	1	8	2	167	168	2	-2	-1	69	63	
0	0	0	0	25	16	0	6	1	292	294	1	-3	-5	249	267	1	0	1	204	207	1	3	5	110	108	1	8	3	21	23	2	-2	0	187	179	
0	0	0	0	619	643	0	6	1	30	22	1	-3	-4	106	117	1	0	2	498	484	1	3	6	21	7	2	0	-5	33	30	2	-2	-1	105	96	
0	0	0	0	121	113	0	6	2	117	122	1	-3	-3	235	250	1	0	3	83	84	1	4	-5	42	46	2	0	-4	137	145	7	-2	-2	128	133	
0	0	0	0	149	141	0	6	3	54	41	1	-3	-2	151	159	1	0	4	181	192	1	4	-4	281	258	2	0	-3	34	39	2	-2	3	25	1	
0	0	0	0	162	159	0	6	4	242	241	1	-3	-2	353	358	1	0	5	203	212	1	4	-2	160	160	2	0	-2	143	136	2	-2	0	182	182	
0	0	0	0	23	23	0	6	5	110	110	1	-3	0	110	110	1	0	-7	110	114	1	4	-2	160	160	2	0	-2	143	136	2	-2	-1	252	232	
0	0	0	0	349	340	0	6	6	203	203	1	-3	1	53	56	1	0	-6	20	26	1	4	-1	95	82	2	0	-2	81	81	2	-1	-6	32	31	
0	0	0	0	54	44	0	7	1	209	197	1	-3	2	35	25	1	1	-5	286	279	1	4	0	514	527	2	0	-5	-6	22	16	2	-1	-5	71	77
0	0	0	0	23	23	0	7	5	4	15	1	-3	4	23	25	1	1	-5	24	23	1	5	1	10	10	1	7	0	5	261	267	2	-1	-6	34	34
0	0	0	0	76	63	0	7	3	240	246	1	-2	-7	55	46	1	1	-3	604	561	1	4	2	274	283	2	0	-4	63	69	2	-1	-3	459	493	
0	0	0	0	151	143	0	7	-3	151	154	1	-2	-4	49	43	1	1	-2	178	171	1	4	3	67	68	2	0	-3	67	69	2	-1	-2	99	93	
0	0	0	0	70	59	0	7	-2	57	67	1	-2	-5	126	121	1	1	-1	278	261	1	4	4	269	269	2	0	-2	26	21	2	-1	-1	585	569	
0	0	0	0	390	391	0	7	1	104	104	1	-2	-4	38	43	1	0	-2	158	147	1	4	4	138	138	2	0	-1	43	45	2	-1	0	170	170	
0	0	0	0	61	61	1	-6	-5	26	24	1	-2	-3	9	21	1	1	1	765	677	1	4	4	140	138	2	0	-5	0	48	67	2	-1	1	249	247
0	0	0	0	201	205	1	-6	-4	96	106	1	-2	-2	488	503	1	1	2	123	126	1	5	4	24	24	2	0	-5	1	139	132	2	-1	2	10	9
0	0	0	0	28	32	1	-6	-3	20	14	1	-2	-1	147	143	1	1	3	128	149	1	5	-3	114	109	2	0	-4	-7	-5	43	2	-1	3	231	251
0	0	0	0	323	311	1	-6	-2	221	232	1	-2	0	409	394	1	1	4	106	105	1	5	-2	95	93	2	0	-4	-6	244	246	2	-1	4	61	71
2	0	-7	58	58	2	3	-2	74	67	2	7	0	26	23	3	-2	3	34	37	3	2	1	34	37	3	6	0	68	64	4	-1	2	25	24		
2	0	-6	109	101	2	3	0	316	324	2	7	1	143	139	3	-1	-7	70	93	3	2	2	14	24	3	6	1	88	80	4	-1	-7	222	205		
2	0	-5	125	101	2	3	0	41	54	2	7	2	40	40	3	-1	-6	103	97	3	2	3	21	18	3	6	2	277	278	4	-1	-6	32	33		
2	0	-4	402	449	2	3	1	540	546	2	7	3	277	276	3	0	-2	24	23	3	2	3	36	22	3	6	3	36	22	4	-1	-6	32	33		
2	0	-3	107	109	2	3	2	200	190	2	7	4	21	16	3	-1	-4	38	39	3	3	-7	200	203	3	6	4	103	100	4	-1	-8	84	87		
2	0	-2	46	93	2	3	3	64	93	2	8	1	61	72	3	-1	-3	171	176	3	3	-6	24	14	3	7	4	20	22	4	-1	-3	243	244		
2	0	-1	189	242	2	3	4	68	81	2	8	0	161	161	3	-1	-2	104	102	3	3	-5	155	146	3	7	3	224	227	4	-1	-2	112	118		
2	0	0	643	640	2	3	5	202	199	2	8	1	17	17	3	-1	-2	103	118	3	3	-4	132	132	3	7	3	17	17	4	-1	-3	159			

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. Although some of the relative absorption corrections were quite large, they were justified by the low errors and reasonable thermal parameters of the resulting refinement (*vide infra*).

Determination and Refinement of the Structure

A straightforward analysis of the Patterson map revealed the positions of the two heavy atoms in the asymmetric unit. A least-squares refinement in the centric space group $P\bar{1}$ and a difference Fourier synthesis were then calculated, using a copper atom in the position which contributed most strongly to the Patterson map and a vanadium atom in the other position. The positions of the three intense image peaks in the difference Fourier map revealed the oxygen atoms.

Three cycles of least-squares refinement (5) of these positions, using a $1/\sigma^2$ weighting scheme, zerovalent scattering factors for Cu, V and O (6), isotropic temperature factors, and corrections for secondary extinction and anomalous dispersion, yielded a residual $R = 0.066$ and a weighted residual $R_w = 0.084$. The anisotropic refinement, based on a data:parameter ratio of 18.7 with 47 independently varied parameters, yielded a final $R = 0.055$ and $R_w = 0.070$ for the observed data. Calculated and observed structure factors are listed in Table I. In the final refinement, the

maximum extinction correction (7) was 23% of $|F_c|$ for the 011 reflection.

Table II presents the final atomic co-ordinates and anisotropic thermal parameters.

Discussion

The structure of the mineral ilmenite, FeTiO_3 (space group $R\bar{3}$), can be described (8) 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 so that each octahedron containing an iron ion shares a face with a titanium octahedron above or below it (but not both) and also shares edges with three other iron octahedra in the same layer. Titanium 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–Fe–vacancy–Fe–Ti–vacancy–*etc.*

$\text{CuVO}_3(\text{I})$ contains distorted hexagonally close-packed oxygen layers such that the ac plane of the triclinic unit cell corresponds to the ideally close-packed array of the ab plane in the hexagonal ilmenite unit cell. The sequence of cations is as in ilmenite: Cu–V–vacancy–V–Cu–vacancy–*etc.* along the pseudohexagonal c axis. The unlike metal ions in the face-sharing octahedra of alternate layers repel each other so that they are further apart than the like metals of edge-sharing octahedra within a layer. These features are clearly seen in Fig. 1, which is a view of the structure perpendicular to the pseudohexagonal c axis. The number beside each thermal ellipsoid (98%) gives its distance in Angstroms above or below the plane of the figure, which is very nearly parallel to the triclinic (111) plane.

Table III lists the pertinent bond distances, angles and polyhedral edge lengths. The copper

TABLE II

$\text{CuVO}_3(\text{I})$: FRACTIONAL ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS^a

Atom	$10^4 x$	$10^4 y$	$10^4 z$	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	2214(1)	4290(1)	3612(1)	1.12(2)	0.89(2)	0.89(2)	-0.63(2)	0.62(2)	-0.44(2)
V	2087(2)	9368(1)	8520(2)	0.86(3)	0.55(3)	0.73(3)	-0.32(2)	0.38(2)	-0.19(2)
O(1)	3546(8)	2248(6)	717(8)	1.13(10)	0.68(9)	1.04(10)	-0.56(8)	0.64(9)	-0.46(8)
O(2)	112(8)	7636(6)	5628(7)	0.90(9)	0.82(9)	0.71(9)	-0.48(8)	0.41(8)	-0.24(7)
O(3)	2734(7)	7679(6)	2073(7)	0.82(9)	0.71(9)	0.59(9)	-0.29(7)	0.29(8)	-0.06(7)

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

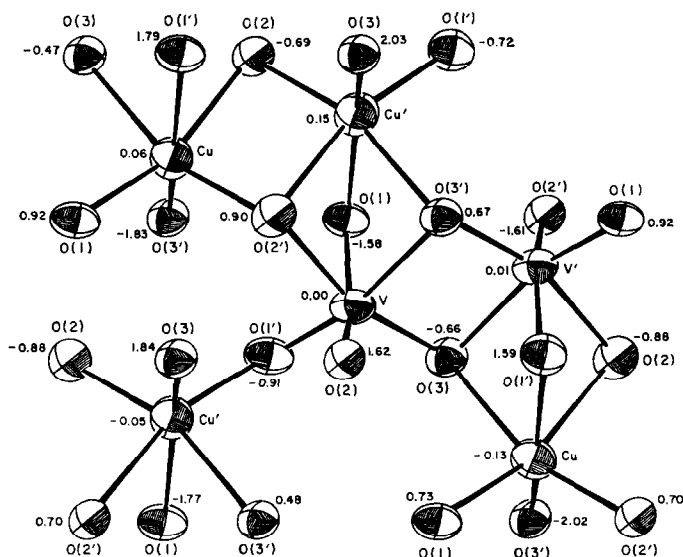


FIG. 1. The structure of CuVO₃(I) as viewed perpendicular to the pseudo-hexagonal *c* axis. The number beside each atom gives its distance in Å above or below the plane of the figure, which is nearly parallel to the triclinic (111) plane.

ion is in a highly distorted six-coordinated polyhedron with an average Cu–O bond distance of 2.129 Å while the vanadium polyhedron has three bond distances of approximately 1.80 Å and three of approximately 2.08 Å; the average V–O bond distance is 1.935 Å. Using the ionic radius for the four-coordinated oxygen ion derived by Shannon and Prewitt (9), the ionic radii for copper and vanadium in CuVO₃(I) are 0.75 and 0.56 Å, respectively. Shannon and Prewitt (9) report radii for the six-coordinated cations as follows: Cu⁺, 0.96; Cu²⁺, 0.73; V⁴⁺, 0.59; V⁵⁺, 0.54 Å; four-coordinated oxygen has a radius of 1.38 Å. On the basis of our interatomic distances the copper in this structure is certainly in the divalent state; therefore, vanadium must be in the 4⁺ state. This conclusion is in agreement with the magnetic data for CoVO₃(I) (1), NiVO₃(I) (2), and MnVO₃(I) (3), which indicate a M²⁺V⁴⁺O₃ ionic distribution in the paramagnetic state.

CuVO₃(I) has an anomalously low paramagnetic moment— $p_{\text{eff}}^2 = 1.26$ (BM)² vs a calculated spin moment of 6 (BM)² for Cu²⁺V⁴⁺O₃ (1). Explanations based on an equilibrium with the valence state Cu⁺V⁵⁺O₃ or the postulate (1) that homopolar V⁴⁺–V⁴⁺ bonding between vanadium ions in *alternate* layers reduces the effective magnetic moment must be discounted on the basis of our crystallographic analysis.

A clue to the nature of this magnetic behavior

lies in the metal–metal distances in the triclinic phase. The Cu–V distance between face-shared polyhedra is 2.972 Å; each copper atom has three other copper atoms linked by edge-shared polyhedra in the *ac* plane at distances of 2.878, 2.951 and 2.997 Å, and each vanadium has three vanadium atoms at distances of 2.922, 2.925 and 2.929 Å in this basal plane (estimated standard deviations are 0.001 Å).

Goodenough (10) has proposed a critical cation–cation distance (R_c) which separates the behavior of valence electrons into two distinct areas: if R (the actual cation–cation separation) is greater than R_c , the electrons behave as *localized* quasiparticles but if $R < R_c$, the electrons become *delocalized* with the occurrence of homopolar cation–cation interaction. In V₂O₃, which has the corundum structure (the ilmenite structure with all metal atoms alike; space group $R\bar{3}c$), the anomalously large *c/a* ratio (in the hexagonal unit cell) is attributed to V³⁺–V³⁺ interactions in the basal plane (11); the V–V distance is 2.88 Å, which is less than the critical distance for V³⁺, $R_c = 2.94$ Å. The postulated R_c for V⁴⁺ is also 2.94 Å (12), which is greater than the average V–V distance in the basal plane for CuVO₃(I) of 2.925 Å. This suggests delocalized metal–metal interactions (itinerant electron antiferromagnetism) in the basal plane, which would decrease the moment of the vanadium ions (13). The three V–V distances are remarkably similar for a struc-

TABLE III

CuVO₃(I): BOND DISTANCES, POLYHEDRAL
EDGE LENGTHS AND BOND ANGLES^a

(i) Interatomic distances (Å)			
Cu-O(1)	1.984(3)	V-O(1)	2.079(3)
-O(2)	2.161(3)	-O(2)	1.814(3)
-O(3)	2.148(3)	-O(3)	1.789(3)
-O(1')	2.372(3)	-O(1')	1.776(3)
-O(2')	2.009(3)	-O(2')	2.071(3)
-O(3')	2.103(3)	-O(3')	2.079(3)
Cu octahedron		V octahedron	
O(1)-O(3)	2.901(4)	O(1)-O(3)	2.803(4)
O(1)-O(1')	3.185(6)	O(1)-O(1')	2.524(6)
O(1)-O(2')	3.099(4)	O(1)-O(2')	2.724(5)
O(1)-O(3')	3.109(5)	O(1)-O(3')	2.708(5)
O(2)-O(3)	2.644(4)	O(2)-O(3)	2.782(6)
O(2)-O(1')	2.724(5)	O(2)-O(1')	2.795(4)
O(2)-O(2')	2.949(6)	O(2)-O(2')	2.572(6)
O(2)-O(3')	3.050(4)	O(2)-O(3')	2.839(4)
O(3)-O(1')	2.708(5)	O(3)-O(1')	2.797(4)
O(3)-O(3')	3.129(6)	O(3)-O(3')	2.550(6)
O(1')-O(2')	3.034(4)	O(1')-O(2')	2.816(4)
O(2')-O(3')	3.188(4)	O(2')-O(3')	2.644(4)
(ii) Angles (deg)			
Cu octahedron		V octahedron	
O(1)-Cu-O(3)	89.1(1)	O(1)-V-O(3)	92.6(1)
O(1)-Cu-O(1')	93.5(1)	O(1)-V-O(1')	81.4(1)
O(1)-Cu-O(2')	101.8(1)	O(1)-V-O(2')	82.1(1)
O(1)-Cu-O(3')	99.0(1)	O(1)-V-O(3')	81.2(1)
O(2)-Cu-O(3)	75.7(1)	O(2)-V-O(3)	101.1(1)
O(2)-Cu-O(1')	73.7(1)	O(2)-V-O(1')	102.2(1)
O(2)-Cu-O(2')	90.0(1)	O(2)-V-O(2')	82.6(1)
O(2)-Cu-O(3')	91.3(1)	O(2)-V-O(3')	93.3(1)
O(3)-Cu-O(1')	73.4(1)	O(3)-V-O(1')	103.4(1)
O(3)-Cu-O(3')	94.8(1)	O(3)-V-O(3')	82.1(1)
O(1')-Cu-O(2')	87.3(1)	O(1')-V-O(2')	93.8(1)
O(2')-Cu-O(3')	101.7(1)	O(2')-V-O(3')	79.1(1)
O(3)-Cu-O(2')	158.5(1)	O(3)-V-O(2')	161.0(1)
O(1)-Cu-O(2)	162.3(1)	O(1')-V-O(3')	162.0(1)
O(1')-Cu-O(3')	162.7(1)	O(1)-V-O(2)	164.5(1)

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

ture of such low symmetry (compare these with the Cu-Cu distances) indicating the symmetric delocalization of vanadium electrons throughout the *ac* plane. Reference to the Figure indicates that the anisotropic thermal ellipsoids of vibration for the vanadium atoms are extended in the basal plane rather than towards oxygen atoms—further indication of cation-cation interaction.

The question then arises as to why the apparently isostructural *M*VO₃(I) compounds (*M* = Mn²⁺, Co²⁺, Ni²⁺) do not exhibit this reduced paramagnetic moment (1-3). If one determines the average parameters of the pseudorhombohedral unit cells for these four compositions and then calculates the *c/a* ratios for the pseudo-hexagonal cells, the *M* = Mn²⁺, Co²⁺ and Ni²⁺ compounds have *c:a* ratios of 2.80 while CuVO₃(I) has a *c/a* ratio of 2.87. Recalling that for these rhombohedral structure-types a larger *c/a* ratio is indicative of metal-metal interaction in the basal plane, this suggests that the V-V distances in the three other compounds are greater than the 2.92 Å distance in CuVO₃(I) and, indeed, probably larger than *R_c* for V⁴⁺ interaction. A complete structural investigation of a second compound in this series would be necessary to confirm this, but the anomalously high *c/a* ratio for CuVO₃(I) together with the paramagnetic data support this conclusion.

This new triclinic distortion of the ilmenite structure type seems to be confined to compositions containing V⁴⁺. The only other vanadium-containing compound with this stoichiometry, FeVO₃, has a disordered corundum structure and has been shown by Mössbauer effect spectroscopy (14) to have the valence distribution Fe³⁺V³⁺O₃.

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