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Phase Equilibrium Study of the System CuV_2O_5–V_2O_4–V_2O_5

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The phase diagram of the system CuV_2O_5–V_2O_4–V_2O_5 at 923 K was established. Two new phases, $Cu_xV_9O_{22}$ ($0.87 \leq x \leq 1.73$) and $Cu_xV_{12}O_{29}$ ($1.0 \leq x \leq 1.9$), were found instead of the oxygen-deficient β'-$Cu_xV_2O_5$ reported earlier. Including β'-$Cu_xV_2O_5$, they form a homologous series of bronze phases $Cu_xV_{6n}O_{15n-m}$. These phases are closely related to β- and β'-$Li_xV_{6n}O_{15n-m}$ found previously. Factors bounding the maximum M content in $M_xV_{6n}O_{15n-m}$ (M = Cu, Li) are discussed. The dc conductivities along the b-axis of the single crystals of the new phases were measured.

Introduction

Vanadium bronzes, $M_xV_2O_5$, crystallize in various types of structures depending on the element M and its content x. In the $Cu_xV_2O_5$ system, three bronze phases are known, $\alpha(0 < x \leq 0.02)$, $\beta'(0.26 \leq x \leq 0.64)$, and $\varepsilon(0.85 \leq x \leq 1)$ (*1*). Mori *et al.* reported a phase diagram of the system Cu_2O–V_2O_4–V_2O_5 in which the β' phase appeared as a phase $Cu_xV_2O_{5-y}$ ($0 \leq y \leq 0.2$) with a large number of oxygen defects (*2*). The phase diagram of the corresponding LiV_2O_5–V_2O_4–V_2O_5 system determined by Takayama-Muromachi and Kato (*3*), however, differs from the diagram of the Cu-containing system by Mori *et al.* Takayama-Muromachi and Kato found a series of vanadium bronzes, β- and β'-$Li_xV_{6n}O_{15n-m}$ (*4*) and concluded that earlier studies (*5*) had misidentified $Li_xV_9O_{22}$ ($n = 3$, $m = 1$ in the above notation) and/or $Li_xV_{12}O_{29}$ ($n = 2$, $m = 1$) as the oxygen-deficient β phase $Li_xV_2O_{5-y}$. The member with $n = 1$ and $m = 0$ corresponds to the well-known β- or β'-$Li_xV_2O_5$. Since the ionic radii of Cu^+ and Li^+ are very close to each other (*6*), their results cast doubt on the phase diagram reported by Mori *et al.* We reinvestigated the phase equilibrium relations in the CuV_2O_5–V_2O_4–V_2O_5 system at 923 K and found that there exist, instead of the oxygen-deficient β' phase, two new bronze phases $Cu_xV_9O_{22}$ and $Cu_xV_{12}O_{29}$. The dc conductivity data for these Cu-based bronze phases were obtained.

Experiment

V_2O_4 was prepared by heating an equimolar mixture of V_2O_5 (99.9%) and V_2O_3 in a sealed silica tube at 1273 K for 3 days. The V_2O_3 had been obtained by reducing the V_2O_5 in hydrogen at 1073 K. Cu_2O was prepared by reducing CuO (99.9%) in air at 1333 K for 1 day and then quenching it in

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liquid nitrogen. The three compounds, V_2O_5, V_2O_4, and Cu_2O, were mixed in the desired ratio in an agate mortar. About 1.5 g of the mixture was sealed in a silica tube and heated at 923 ± 2 K for 48–72 hr, then cooled in air. The product was ground and examined by powder X-ray diffraction using Cu$K\alpha$ radiation. This procedure was repeated until the powder X-ray pattern did not change anymore. Usually, one heating run was enough to obtain steady state, but the formation of the $Cu_xV_9O_{22}$ phase was somewhat sluggish and two runs of prolonged heating (both 168–192 hr) were needed for the $Cu_xV_9O_{22}$-containing region to reach equilibrium. Single crystals of the newly discovered bronze phases were prepared by chemical transport methods, using as carriers HCl gas for $Cu_xV_{12}O_{29}$ and Cl_2 gas for $Cu_xV_9O_{22}$. Typical size of the crystals obtained was 0.6 × 0.4 × 5.0 mm. The dc conductivities along the *b*-axis of the single crystals of $Cu_xV_9O_{22}$ and $Cu_xV_{12}O_{29}$ were measured by the standard four-probe method.

Results and Discussion

The phase diagram determined in the present study is shown in Fig. 1. The phase relations in the $Cu_xV_2O_5$ system are identical with the earlier results (*1*) except for minor differences. There are three bronze phases, α-, β'-, and ε-$Cu_xV_2O_5$. The α phase is based on the parent oxide V_2O_5 with the Cu ions inserted between V_2O_5 layers, while in the other phases, major structural rearrangement occurs in the V_2O_5 framework (*7*). The compositional range of the α phase is very narrow and that in Fig. 1 was taken from the previous report (*1*). The compositional range of the β' phase was determined to be $0.237 \leq x \leq 0.686$ by the variation of a lattice constant (β angle) with copper content x (see Fig. 2a). Of the four experimental points ($Cu_xV_2O_5$, $x = 0.7$, 0.8, 0.9, and 1.0) covering the ε-$Cu_xV_2O_5$ region, the samples with $x = 0.8$ and 0.9 were single-phased, while the sample with $x = 0.7$ contained the β' phase in addition to the ε phase and the sample with $x = 1.0$ was a mixture of the ε phase, Cu_3VO_4, and V_2O_4. Thus, we estimated the range of the ε phase to be $0.75 \leq x \leq 0.95$. The range of the β' phase is in good agreement with the previous result $0.26 \leq x \leq 0.64$ (*1*), whereas that of the ε phase is substantially different from the previous one, $0.85 \leq x \leq 1$. In particular, we could not obtain the "stoichiometric" ε phase, CuV_2O_5, at least at 923 K.

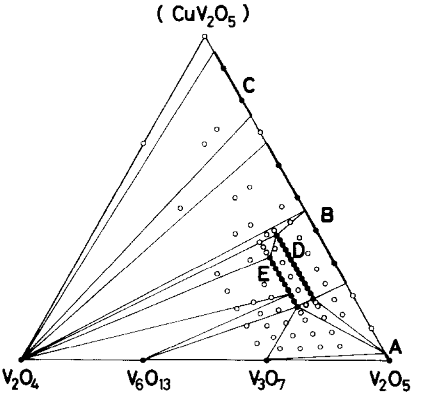

FIG. 1. Phase diagram of the CuV_2O_5–V_2O_4–V_2O_5 system at 923 K (A) α-$Cu_xV_2O_5$, (B) β'-$Cu_xV_2O_5$, (C) ε-$Cu_xV_2O_5$, (D) $Cu_xV_9O_{22}$, (E) $Cu_xV_{12}O_{29}$. Circles indicate experimental points. Solid circles show the single-phased points. Open circles show the multiphased points.

In addition to these three bronze phases, we found two compounds in the oxygen-poor region; they were $Cu_xV_9O_{22}$ and $Cu_xV_{12}O_{29}$. The Weissenberg photographs and powder X-ray patterns taken for them indicated that the $Cu_xV_9O_{22}$ and the $Cu_xV_{12}O_{29}$ have the same space groups and almost the same lattice parameters (see Fig. 2) as the β- (or β'-) $Li_xV_9O_{22}$ (monoclinic with SG $P2_1/m$) and β- (or β'-) $Li_xV_{12}O_{29}$ (monoclinic with SG $C2/m$), respectively; i.e., there exists a series of copper vanadium bronzes $Cu_xV_{6n}O_{15n-m}$ (for the β'-

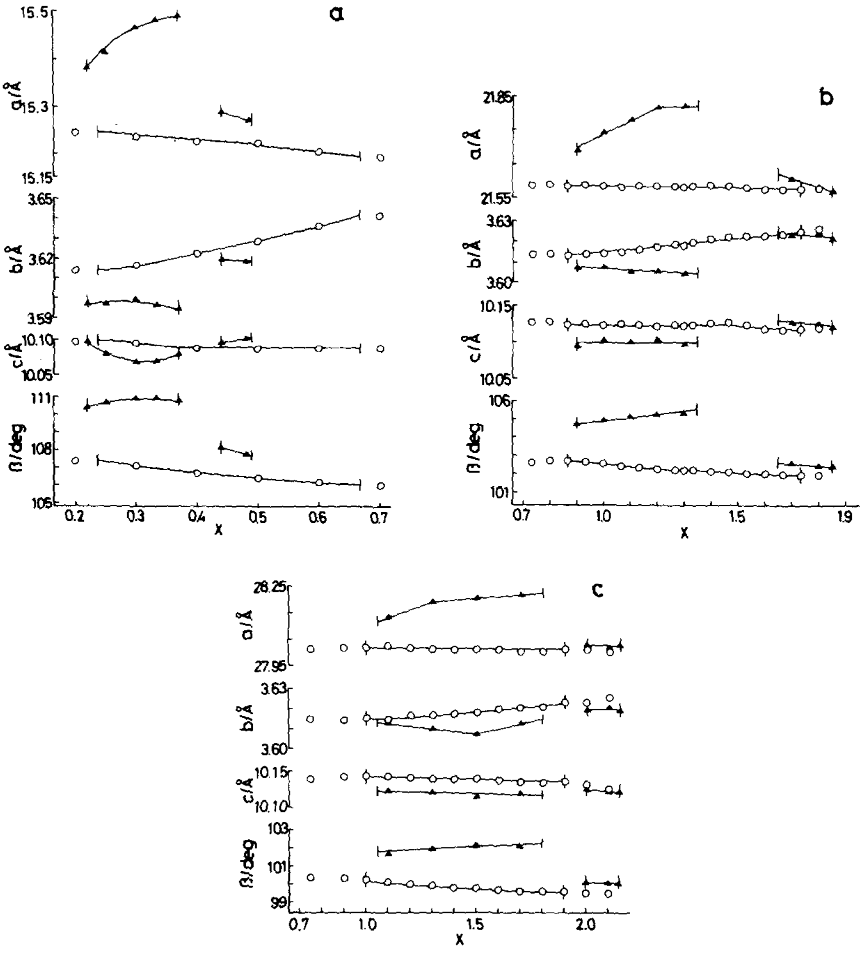

FIG. 2. Lattice parameters versus x for the systems (a) $M_xV_2O_5$, (b) $M_xV_9O_{22}$, and (c) $M_xV_{12}O_{29}$. (○) M = Cu, (▲) M = Li.

$Cu_xV_2O_5$, $n = 1$ and $m = 0$) corresponding to $Li_xV_{6n}O_{15n-m}$. Tables I–III show the powder X-ray patterns of representative compounds. Table IV shows their lattice parameters. The single-crystal X-ray analysis was completed for $Cu_xV_{12}O_{29}$ (*8*) and is in progress for $Cu_xV_9O_{22}$. Detailed structural parameters will be published soon.

Mori *et al.* reported the phase relations of the Cu_2O–V_2O_4–V_2O_5 system determined at 893 K (*2*). In their diagram, the homogeneity region of "β'-$Cu_xV_2O_5$" covers a wide area due to "oxygen deficiency," where in our diagram (Fig. 1) the $Cu_xV_{12}O_{29}$ phase would exist. Since their experimental temperature is close to the present one, it is unlikely that the phase relations are so different from those of the study. We suggest that they misidentified the $Cu_xV_9O_{22}$ and $Cu_xV_{12}O_{29}$ phases as the oxygen deficient β' phase, $Cu_xV_2O_{5-y}$.

The overall aspect of the present phase diagram resembles very closely that of the LiV_2O_5–V_2O_4–V_2O_5 system, which seems to be owing to the similar ionic radii of Cu^+ and Li^+. There is, however, a notable dif-

TABLE I

POWDER X-RAY PATTERN OF $\beta' Cu_{0.4}V_2O_5$

h	k	l	d_{obs}(Å)	d_{calc}(Å)	I/I_0	h	k	l	d_{obs}(Å)	d_{calc}(Å)	I/I_0
0	0	1	9.566	9.662	13	5	1	−4	1.8775	1.8774	<1
2	0	0	7.242	7.291	100	7	1	−1	1.8601	1.8607	2
2	0	−1	6.797	6.840	2	8	0	0	1.8222	1.8229	1
0	0	2	4.814	4.831	9	0	2	0	1.8102	1.8110	2
2	0	−2	4.677	4.695	1	6	0	−5	1.7815	1.7820	1
4	0	−1	3.7842	3.7888	2	2	0	5	1.7472	1.7480	<1
4	0	0	3.6414	3.6457	4	6	0	3	1.7171	1.7176	3
2	0	2	3.5787	3.5820	6	8	0	−4	1.7093	1.7099	1
1	1	0	3.5103	3.5153	1	5	1	3	1.6867	1.6873	1
1	1	−1	3.3765	3.3794	5	2	0	−6	1.6773	1.6771	<1
1	1	1	3.2296	3.2324	1	5	1	−5	1.6672	1.6672	<1
4	0	1	3.1245	3.1275	67	0	0	6	1.6105	1.6104	2
1	1	−2	2.9401	2.9409	1	8	0	2	1.5632	1.5638	4
3	1	−1	2.9213	2.9230	<1	4	0	5	1.5350	1.5349	2
4	0	−3	2.8526	2.8540	18	4	2	−3	1.5291	1.5291	1
1	1	2	2.7519	2.7533	<1	9	1	−1	1.5236	1.5229	3
3	1	−2	2.6999	2.7021	3	10	0	−2	1.5216	1.5221	4
2	0	3	2.6748	2.6761	2	6	0	4	1.5104	1.5103	<1
2	0	−4	2.5179	2.5189	1	5	1	4	1.4964	1.4964	2
1	1	−3	2.4596	2.4610	<1	2	0	6	1.4854	1.4853	2
0	0	4	2.4146	2.4156	7	9	1	0	1.4788	1.4791	1
4	0	−4	2.3467	2.3475	2	5	1	−6	1.4788	1.4789	1
1	1	3	2.2957	2.2970	1	10	0	0	1.4580	1.4583	<1
5	1	0	2.2702	2.2717	2	10	0	−4	1.4452	1.4453	1
6	0	1	2.2105	2.2117	16	4	0	−7	1.4342	1.4344	1
4	0	3	2.1289	2.1296	1	4	2	−4	1.4342	1.4339	1
5	1	−3	2.0893	2.0892	1	8	0	−6	1.4273	1.4270	<1
2	0	−5	2.0162	2.0168	2	9	1	1	1.4078	1.4079	2
6	0	2	1.9562	1.9574	7	6	2	1	1.4009	1.4012	1
4	0	−5	1.9562	1.9553	7	10	0	1	1.3842	1.3845	1
1	1	4	1.9294	1.9296	<1	9	1	−5	1.3587	1.3588	1
8	0	−2	1.8938	1.8944	5						

ference; in the Li-containing system (*3*, *9*), there exist two closely related but different phases, β- and β'-$Li_xV_2O_5$, β- and β'-$Li_xV_9O_{22}$, or β- and β'-$Li_xV_{12}O_{29}$, corresponding to the one-phase region of β'-$Cu_xV_2O_5$, $Cu_xV_9O_{22}$, or $Cu_xV_{12}O_{29}$, respectively (see below).

Figures 2a–2c show lattice parameters of the $M_xV_{6n}O_{15n-m}$-type bronze phases (M = Li and Cu) as functions of x. The data of the Li-containing phases were cited from the previous reports (*3*, *9*). For every $Li_xV_{6n}O_{15n-m}$ system, there is a two-phase region across which the lattice parameters change abruptly. The Li-poor phase has been termed β and the Li-rich phase β'. In contrast, the lattice parameters of the Cu-containing phases change smoothly with x and the two-phase region is not present within any $Cu_xV_{6n}O_{15n-m}$ systems. Comparing the Li and Cu systems, it is seen that the lattice parameters of every Cu system are closer to those of the corresponding Li-rich phase (β' phase) than to those of the β phase.

β- and β'-$M_xV_2O_5$ (M = Cu, Li) (*7–11*)

TABLE II

POWDER X-RAY PATTERN OF $Cu_{1.3}V_9O_{22}$

h	k	l	d_{obs}(Å)	d_{calc}(Å)	I/I_0	h	k	l	d_{obs}(Å)	d_{calc}(Å)	I/I_0
0	0	1	9.799	9.893	10	11	0	−2	1.9298	1.9303	2
3	0	0	6.985	7.030	100	10	1	−1	1.8525	1.8530	1
3	0	−1	6.371	6.405	2	8	1	2	1.8457	1.8455	<1
0	0	2	4.929	4.946	4	10	1	0	1.8217	1.8219	<1
1	0	2	4.588	4.604	2	0	2	0	1.8086	1.8086	2
5	0	−1	4.2076	4.2144	<1	12	0	−2	1.7784	1.7788	1
2	0	2	4.1508	4.1535	<1	8	0	−5	1.7723	1.7724	<1
3	0	2	3.6924	3.6946	4	12	0	0	1.7570	1.7574	1
6	0	−1	3.5544	3.5576	1	3	2	0	1.7516	1.7516	<1
6	0	0	3.5113	3.5148	6	9	0	3	1.7439	1.7440	1
1	1	−1	3.3926	3.3929	4	9	1	2	1.7251	1.7255	<1
1	1	1	3.3108	3.3164	<1	11	0	−4	1.6989	1.6990	1
4	0	2	3.2756	3.2783	1	2	0	−6	1.6846	1.6842	<1
1	0	3	3.1595	3.1578	1	8	1	3	1.6645	1.6646	<1
6	0	1	3.1091	3.1111	56	13	0	−2	1.6480	1.6480	<1
7	0	0	3.0110	3.0127	1	10	0	3	1.6275	1.6274	1
4	1	0	2.9825	2.9827	<1	1	0	6	1.6173	1.6174	1
1	1	−2	2.9424	2.9425	<1	6	2	1	1.5635	1.5636	1
5	0	−3	2.9120	2.9137	8	12	0	2	1.5553	1.5556	2
3	0	3	2.7679	2.7690	1	9	0	4	1.5456	1.5458	<1
2	1	2	2.7270	2.7278	<1	14	0	−1	1.5377	1.5384	1
4	1	−2	2.6999	2.7010	2	14	0	−2	1.5341	1.5342	2
8	0	0	2.6341	2.6361	1	3	1	−6	1.5286	1.5285	1
3	1	2	2.5818	2.5847	<1	4	1	−6	1.5226	1.5221	<1
4	0	3	2.5631	2.5629	<1	7	0	5	1.5135	1.5136	1
2	0	−4	2.5286	2.5296	1	13	1	−1	1.5068	1.5070	1
0	0	4	2.4725	2.4732	1	8	1	4	1.4930	1.4930	1
1	1	−3	2.4638	2.4651	<1	6	1	−6	1.4869	1.4869	2
1	0	4	2.3973	2.3984	4	4	0	6	1.4869	1.4867	2
5	0	−4	2.3618	2.3623	1	13	1	0	1.4799	1.4802	<1
9	0	0	2.3423	2.3432	1	13	1	−3	1.4597	1.4596	<1
7	1	0	2.3145	2.3150	1	1	2	4	1.4442	1.4441	<1
2	1	3	2.2959	2.2970	<1	5	0	−7	1.4347	1.4344	<1
9	0	1	2.1783	2.1792	18	12	0	3	1.4307	1.4305	<1
8	1	0	2.1303	2.1304	<1	1	0	−7	1.4307	1.4304	<1
7	1	−3	2.0581	2.0583	<1	13	1	1	1.4242	1.4243	1
2	0	−5	2.0234	2.0237	2	15	0	0	1.4058	1.4059	<1
10	0	1	1.9787	1.9791	<1	9	2	1	1.3917	1.3917	<1
9	0	2	1.9630	1.9632	4	12	1	−5	1.3681	1.3683	<1
5	0	−5	1.9571	1.9573	3	15	0	1	1.3527	1.3527	1
2	1	4	1.9421	1.9422	<1	2	2	−5	1.3483	1.3485	<1

have essentially the same V–O framework as the well-known β-$Na_xV_2O_5$ (*12*) and have one kind of tunnel (denoted A in Fig. 3) along the *b*-axis. Within the tunnel, there are two kinds of *M* ion sites: one is a seven-coordinated site and the other is a five-coordinated site; the two are separated from each other by *b*/2. In β-$Li_xV_2O_5$ (*10*), isostructural with β-$Na_xV_2O_5$, Li^+ ions occupy the "seven-coordinated sites" (hereafter we will call them β-type sites.). However, in the β′-$Cu_xV_2O_5$ (*7, 11*), Cu^+ ions occupy

TABLE III

POWDER X-RAY PATTERN OF $Cu_{1.5}V_{12}O_{29}$

h	k	l	d_{obs}(Å)	d_{calc}(Å)	I/I_0	h	k	l	d_{obs}(Å)	d_{calc}(Å)	I/I_0
0	0	1	9.897	9.992	27	8	0	−5	1.8716	1.8719	1
4	0	0	6.861	6.901	82	13	1	−1	1.8494	1.8498	4
4	0	−1	6.160	6.188	10	13	1	0	1.8313	1.8314	2
0	0	2	4.979	4.996	14	11	1	2	1.8194	1.8192	2
6	0	0	4.587	4.601	1	0	2	0	1.8086	1.8090	9
2	0	2	4.449	4.463	7	10	0	−5	1.7666	1.7667	2
4	0	2	3.7539	3.7568	13	12	0	3	1.7588	1.7590	3
8	0	0	3.4491	3.4507	10	4	2	0	1.7497	1.7499	1
1	1	−1	3.3983	3.4001	30	16	0	−2	1.7240	1.7231	3
2	0	−3	3.3696	3.3702	2	14	0	−4	1.6931	1.6931	6
1	1	1	3.3509	3.3530	4	2	0	−6	1.6876	1.6876	1
3	1	−1	3.2507	3.2522	3	11	1	3	1.6536	1.6536	2
4	0	−3	3.2187	3.2201	5	13	1	2	1.6439	1.6439	1
6	0	2	3.1302	3.1312	7	2	0	6	1.6209	1.6211	4
8	0	1	3.1022	3.1040	100	14	0	3	1.5835	1.5836	2
5	1	0	3.0243	3.0261	2	8	2	1	1.5627	1.5629	4
5	1	−1	2.9702	2.9736	2	16	0	2	1.5519	1.5520	4
6	0	−3	2.9424	2.9446	57	11	1	−5	1.5464	1.5464	3
4	0	3	2.8173	2.8191	4	18	0	−2	1.5408	1.5410	8
10	0	0	2.7592	2.7606	2	3	1	−6	1.5308	1.5308	6
3	1	2	2.7148	2.7155	3	5	1	−6	1.5194	1.5197	1
5	1	−2	2.7000	2.7016	15	10	0	5	1.5028	1.5027	4
8	0	−3	2.6277	2.6286	6	17	1	−1	1.4995	1.4994	4
2	0	−4	2.5329	2.5343	9	11	1	4	1.4917	1.4919	11
6	0	3	2.5040	2.5045	3	6	0	6	1.4876	1.4876	6
0	0	4	2.4968	2.4981	2	2	2	−4	1.4722	1.4724	1
1	1	−3	2.4669	2.4680	3	13	1	−5	1.4600	1.4603	1
2	0	4	2.3877	2.3884	12	2	2	4	1.4418	1.4421	1
6	0	−4	2.3687	2.3696	8	17	1	−3	1.4382	1.4384	2
9	1	0	2.3388	2.3396	5	17	1	1	1.4337	1.4338	4
10	0	−3	2.3266	2.3274	2	0	0	7	1.4277	1.4275	1
3	1	3	2.2973	2.2980	3	18	0	−4	1.4187	1.4182	1
8	0	3	2.2160	2.2167	2	8	0	−7	1.4058	1.4056	1
12	0	1	2.1626	2.1634	32	14	0	−6	1.3942	1.3936	1
11	1	0	2.0617	2.0621	2	12	2	1	1.3879	1.3878	2
9	1	−3	2.0421	2.0423	2	20	0	0	1.3805	1.3803	1
2	0	−5	2.0262	2.0270	10	15	1	−5	1.3733	1.3734	3
12	0	2	1.9668	1.9672	9	19	1	−1	1.3648	1.3648	<1
6	0	−5	1.9575	1.9578	21	2	2	−5	1.3497	1.3497	1
14	0	−2	1.9494	1.9501	9	7	1	6	1.3452	1.3451	1

the five-coordinated sites (β'-type site) rather than the β-type sites. It is believed that the Li^+ position in β'-$Li_xV_2O_5$ (10) is also of the β'-type. In $M_xV_9O_{22}$ and $M_xV_{12}O_{29}$ (*8, 13, 14*), there are two types of tunnels along the *b*-axis, denoted by A and B in Fig. 3. Tunnel A is similar to that of β- and β'-$M_xV_2O_5$. Tunnel B has essentially the same site configuration in all of the $M_xV_{6n}O_{15n-m}$ structures and can contain at most one *M* ion per unit cell. It is natural to expect that two phases, β- and β'-$Li_xV_9O_{22}$ (or β- and β'-$Li_xV_{12}O_{29}$), are distinguished by different Li positions in tunnel A. In-

TABLE IV

LATTICE PARAMETERS OF $Cu_xV_{6n}O_{15n-m}$

Compound	a(Å)	b(Å)	c(Å)	β(°)
β'-$Cu_{0.4}V_2O_5$	15.223(1)	3.6221(4)	10.087(1)	106.67(1)
$Cu_{1.3}V_9O_{22}$	21.577(1)	3.6176(4)	10.121(1)	102.20(1)
$Cu_{1.5}V_{12}O_{29}$	28.010(2)	3.6177(3)	10.139(1)	99.73(1)

deed, it was confirmed that the Li position in tunnel A of β-$Li_xV_9O_{22}$ *(13)* or β-$Li_xV_{12}O_{29}$ *(14)* is of the β-type while the Cu position in tunnel A of $Cu_xV_{12}O_{29}$ *(8)* is of the β'-type. However, the Li site in tunnel A of β'-$Li_xV_9O_{22}$ (and β'-$Li_xV_{12}O_{29}$) *(13, 14)* could not be determined by X-ray diffraction methods, suggesting that the Li ions were distributed somewhat randomly.

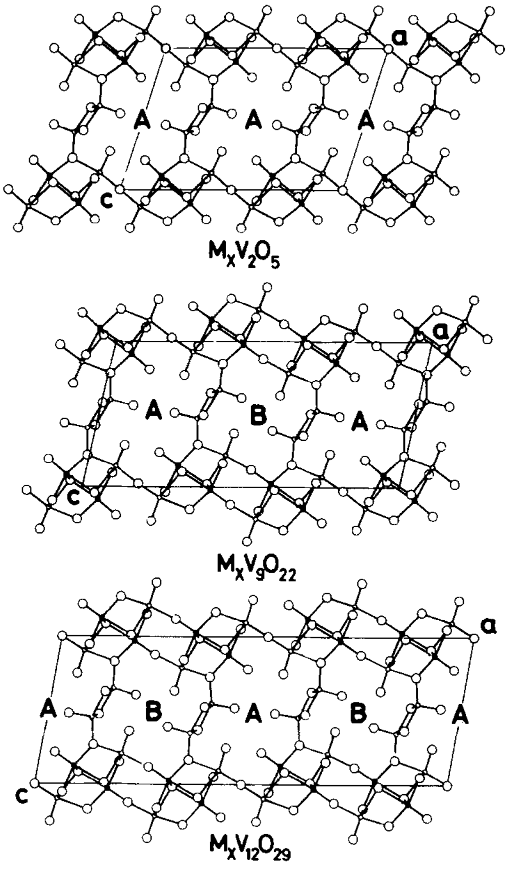

FIG. 3. Projections of the $M_xV_{6n}O_{15n-m}$ (M = Cu, Li) structures onto the (010) plane. Large circles represent oxygen atoms, small circles vanadium atoms. Solid circles indicate possible sites for V^{4+}.

Since the two nearest β-type sites are too close to be occupied simultaneously, tunnel A can contain at most one M ion per unit cell in β-$M_xV_2O_5$ (i.e., maximum x is $\frac{1}{3}$). On the contrary, tunnel A of β'-$M_xV_2O_5$ can contain two M ions per unit cell (i.e., maximum x is $\frac{2}{3}$). If the same consideration is applied to the other members of the present series, the maximum x values may be calculated (including M ions in tunnel B) to be 1.5 for β-$M_xV_9O_{22}$, 2.5 for β'-$M_xV_9O_{22}$, 2.0 for β-$M_xV_{12}O_{29}$, and 3.0 for β'-$M_xV_{12}O_{29}$.

In $M_xV_{6n}O_{15n-m}$, two-thirds of the vanadium atoms are coordinated by six oxygen atoms. The six-coordinated vanadium site can be divided equally into two groups in β- and β'-$M_xV_2O_5$. One of them makes a zigzag chain by itself along the b-axis and is termed the V(1) site (indicated by solid circles in Fig. 3). Goodenough *(15)* suggested that V^{4+} ions in the β- (or β'-)$M_xV_2O_5$ are concentrated at the V(1) sites. His suggestion was confirmed experimentally for β-$Na_xV_2O_5$ *(16, 17)*. On the other hand, Cu atoms are known by ESR study to be monovalent in β'-$Cu_xV_2O_5$ *(18)*. That is to say, x also represents the number of V^{4+} ions per unit formula in β'-$Cu_xV_2O_5$. If we assume that only V ions at the V(1) site can be reduced to V^{4+}, the maximum x becomes $\frac{2}{3}$ which is equal to the number of V(1) sites per unit formula. In $M_xV_9O_{22}$ and $M_xV_{12}O_{29}$, half of the six-coordinated vanadium atoms are at the V(1)-like sites (indicated by solid circles in Fig. 3), and there are three and four of them per unit formula, respectively. It seems reasonable to assume that V ions at these sites are preferably reduced to V^{4+} as in β- and β'-$M_xV_2O_5$. Here we assume that the Cu atoms in every $Cu_xV_{6n}O_{15n-m}$ are monovalent rather than divalent. Since both $Cu_xV_9O_{22}$ and $Cu_xV_{12}O_{29}$ exist in the reduced region more than β'-$Cu_xV_2O_5$ does, the above assump-

TABLE V

RANGE OF x FOR THE SYSTEM $M_xV_{6n}O_{15n-m}$ (M = Cu, Li)

Compound	Range of x (obs)	Maximum x (calc)	
		M site	V^{4+} site
β'-$Cu_xV_2O_5$	0.237–0.686	$\frac{2}{3}$	$\frac{2}{3}$
$Cu_xV_9O_{22}$	0.87–1.73	2.5	2.0
$Cu_xV_{12}O_{29}$	1.0–1.9	3.0	2.0
β'-$Li_xV_2O_5$	0.44–0.49[a]	$\frac{2}{3}$	$\frac{2}{3}$
β'-$Li_xV_9O_{22}$	1.65–1.85[b]	2.5	2.0
β'-$Li_xV_{12}O_{29}$	2.05–2.15[b]	3.0	2.0
β-$Li_xV_2O_5$	0.22–0.37[a]	$\frac{1}{3}$	$\frac{2}{3}$
β-$Li_xV_9O_{22}$	0.90–1.35[b]	1.5	2.0
β-$Li_xV_{12}O_{29}$	1.05–1.80[b]	2.0	2.0

[a] From Ref. (*9*).

[b] From Ref. (*3*).

tion seems reasonable. Taking into account the intrinsic V^{4+} ions included in the hypothetical mother oxides "V_9O_{22}" and "$V_{12}O_{29}$," the upper limit of x bounded by the number of the available "V^{4+} sites" becomes 2.0 for both $M_xV_9O_{22}$ and $M_xV_{12}O_{29}$.

In Table V, we compare the experimental values of maximum x with the calculated values based on the numbers of possible "M sites" and "V^{4+} sites" for various $M_xV_{6n}O_{15n-m}$-type compounds. Table V indicates that the maximum x determined experimentally is close to the smaller one of two calculated values. For instance, in every β-$Li_xV_{6n}O_{15n-m}$, the maximum x based on the V^{4+} site is larger than that based on the Li site and the experimental value is close to the latter. On the contrary, in $Cu_xV_9O_{22}$ or $Cu_xV_{12}O_{29}$, the number of possible V^{4+} sites is less than that of the Cu sites and the maximum Cu content seems to be restricted by the former.

In the system $M_xV_2O_5$ with M = Na^+ (*19*), K^+ (*20*), Ag^+ (*21*), and Pb^{2+} (*22*), which are larger than Cu^+ and Li^+, the β-type phase appears while the β'-type does not. For Li^+, both β- and β'-type phases exist, and for Cu^+, only the β'-type phase is stable. These facts suggest that larger M ions prefer the β-type structure while smaller M ions prefer the β'-type. However, the size of the M ions cannot explain why in the Cu-containing system only the β'-type phase appears, contrary to the case of the Li-containing system and despite the close ionic radii of Li^+ and Cu^+ (*6*). One possible explanation is a unique site preference of the Cu^+ ion; i.e., it prefers a linear two-coordinated site. In the β'-type structure, the M ion is coordinated linearly by two close oxygen atoms with distances ca. 1.8 Å and by three more distant oxygen atoms with distances ca. 2.4 Å (*8, 11*). The former value is close to the ideal distance, 1.86 Å, between two-coordinated Cu^+ and six-coordinated O^{2-} (*6*). The β'-type site can, in a sense, be considered a linear two-coordinated site. On the other hand, the β-type site is far from the linear two-coordinated site. We suggest that is why only the β' phase appears in the $Cu_xV_{6n}O_{15n-m}$.

Figure 4 indicates the dc conductivities along the *b*-axis of single crystals for some $Cu_xV_{6n}O_{15n-m}$ compounds. All samples examined in the present study show semicon-

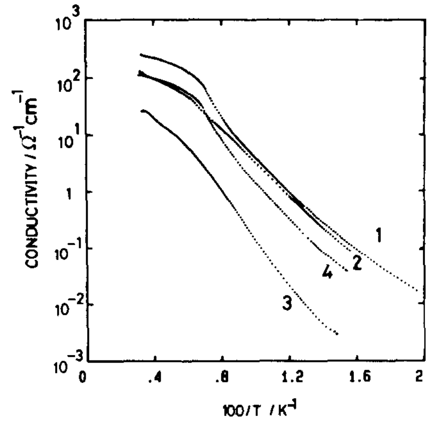

FIG. 4. The dc conductivity along the *b*-axis of the single crystal as a function of reciprocal temperature. (1) $Cu_{1.8}V_{12}O_{29}$, (2) $Cu_{1.5}V_{12}O_{29}$, (3) $Cu_{1.1}V_2O_{29}$, (4) $Cu_{1.6}V_9O_{22}$.

ducting behavior, and the conductivity tends to increase with increasing x for $Cu_xV_{12}O_{29}$. Mori *et al.* obtained single crystals of the Cu-containing bronze phase(s) by slow cooling of melt phases within the CuV_2O_5–V_2O_5–V_2O_4 system and found that some of them retained metallic conductivity down to 1.4 K (*2*). Their results might suggest that there is (are) some other bronze phase(s) besides $Cu_xV_9O_{22}$ and $Cu_xV_{12}O_{29}$ at higher temperatures. Further study is needed to clarify this point.

As seen in Fig. 4, the conductivity of $Cu_{1.8}V_{12}O_{29}$ or $Cu_{1.6}V_9O_{22}$ changes somewhat anomalously at around 140 K ($1/T \approx 0.007$). The anomaly disappears in the Cu-poor compounds, $Cu_{1.5}V_{12}O_{29}$ and $Cu_{1.1}V_{12}O_{29}$. Kanai *et al.* found satellite reflections at low temperatures in X-ray diffraction patterns of β-$Na_{0.33}V_2O_5$, $Li_xV_2O_5$ (x = 0.36, 0.4, 0.525, 0.55), and β'-$Cu_xV_2O_5$ (x = 0.33, 0.4), which indicate the structural phase transition (*23, 24*). They tried to explain the superlattice reflections by an ordering of V^{4+}–V^{4+} pairs in the V(1)–V(1) zigzag chain. Their observation suggests that the anomaly in Fig. 4 may be associated with some structural phase transition. Low-temperature X-ray diffraction measurement is advisable for more detailed discussion.

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