Oxide Chemistry. Part II.[1] Ternary Oxides containing Copper in Oxidation States-I, -II, -III, and -IV

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We report an investigation of the preparation, structure, and magnetic properties of ternary oxides containing copper in oxidation states-I, -II, -III, and -IV. The compounds described are: $ACuO_2$ (A = Al or Ga); $ACuO_2$ (A = Ca, Sr, or Ba), $A_2Cu_2O_5$ (A = Sc, Y, Bi, or In), and A_2CuO_4 (A = La, Al, or Ga); $BaCuO_{2.5}$, $ACuO_3$ (A = Y or La); and $BaCuO_{2.63}$ which is the only phase containing copper(IV) which could be obtained. *X*-Ray powder patterns have been indexed wherever possible and magnetic-susceptibility measurements from 80 to 300 K are interpreted for all paramagnetic species.

WE have recently described[1] studies of ternary oxides containing nickel in oxidation states between II and IV. We now describe complementary studies of the chemistry of copper.

There are no reports in the literature of compounds containing copper(IV), and little is known of the chemistry of copper(III). The compounds K_3CuF_6 and $K_7Cu(IO_6)_2{\cdot}7H_2O$, and the copper(III) oxides ACu_2O_4 (A = Ca, Sr, or Ba) have been prepared in solution,[2-4] but no preparations in the solid state at atmospheric pressure have been described. Recently,[5] $LaCuO_3$ has been prepared from La_2CuO_4 and CuO in an excess of $KClO_3$ at 900 °C and 65 kbar of oxygen. A number of ternary systems containing copper(II) are known: $ACuO_2$ (A = Ca, Sr, or Ba),[6] La_2CuO_4,[7,8] A_2CuO_4 (A = Al or Ga),[9,10] and $In_2Cu_2O_5$.[11] Many ternary systems containing copper(I) are known but we have only prepared $CuAlO_2$ and $CuGaO_2$, both of which have been reported previously.[9,12,13] No magnetic studies of these compounds, apart from La_2CuO_4 and $LaCuO_3$, have been reported.

We have attempted a comprehensive survey of the ternary oxide chemistry of copper, using only solid-state reactions and describe the magnetic properties of the compounds formed, together with analytical studies, including direct determination of oxidation state where-ever possible, as well as *X*-ray powder diffraction and magnetic studies.

RESULTS AND DISCUSSION

(a) *Copper*(I) *Compounds*.—The only compounds containing copper(I) which we have prepared are $CuAlO_2$ and $CuGaO_2$. Both have been prepared previously by thermal decomposition[9] of the spinels $CuAl_2O_4$ and $CuGa_2O_4$, while $CuAlO_2$ has been prepared[12] by heating Cu_2O and $Al(OH)_3$, or the nitrates.[13] We prepared $CuAlO_2$ by heating CuO and Al_2O_3 or $Cu(NO_3)_2$ and $Al(NO_3)_3$ at 1100 °C for 5 days. $CuGaO_2$ was prepared from CuO and Ga_2O_3 at 1180 °C for 7 days. Elemental analyses are listed in Table 1. Both compounds were found to be diamagnetic, confirming their formulation as copper(I) compounds.

In view of the known disproportionation of copper(II) oxide at high temperatures, it may be that many of the compounds described below will disproportionate at high temperatures yielding new copper(I) species. We are investigating this possibility.

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(b) *Copper*(II) *Compounds*.—$CaCuO_2$, $SrCuO_2$, and $BaCuO_2$ were prepared by heating equimolar mixtures of CuO and the alkaline-earth oxide or carbonate at 850 °C for 24, 72, and 48 h respectively. Analyses and mean oxidation-state determinations (see Table 1) support a mean oxidation state of II for copper in these compounds. We cannot exclude the possibility that these compounds contain equal amounts of copper-(I) and -(III) since they are black, preventing spectrosopic determination. A number of arguments favour the presence of copper(II) only: (i) there is no evidence for the formation of copper-(III) at atmospheric pressure, moreover, they would be expected to disproportionate at 850 °C; (ii) it is unlikely, due to the large differences in ionic size of Cu^I and Cu^{III}, that they could be incorporated in a lattice without producing substantial distortions; (iii) the magnetic properties of the compounds reveal some magnetic interaction which would not occur if half the copper atoms were diamagnetic copper(I).

TABLE 1

Analytical data for copper ternary oxides

	Analyses (%)			
	Calculated		Found	
Compound	M	Cu	M	Cu
$CaCuO_2$	29·55	46·85	30·1	47·4
$SrCuO_2$	47·84	34·69	47·3	34·2
$BaCuO_2$	58·97	27·28	58·3	27·7
$BaCuO_{2·1}$	58·57	27·10	58·1	26·9
$BaCuO_{2·5}$ [a]	57·02	26·38	57·3	26·4
$BaCuO_{2·5}$ [b]	57·02	26·38	57·2	26·5
$BaCuO_{2·63}$	56·53	26·15	56·7	26·3
$Sc_2Cu_2O_5$	30·27	42·79	30·2	42·8
$Y_2Cu_2O_5$	46·20	33·02	45·8	33·3
$YCuO_3$	44·35	31·70	44·5	31·9
La_2CuO_4	68·54	15·67	68·3	16·0
$LaCuO_3$	55·46	24·37	55·2	24·5
Al_2CuO_4	29·73	35·01	30·2	34·6
$AlCuO_2$	22·02	51·86	22·4	51·3
Ga_2CuO_4 [c]	52·23	23·80	49·2	24·0
$GaCuO_2$ [c]	42·19	38·45	42·3	38·3
$In_2Cu_2O_5$	52·58	29·10	52·3	29·4
$Bi_2Cu_2O_5$	66·87	20·33	67·2	20·2

[a] Prepared at atmospheric pressure. [b] Prepared at high pressure. [c] Analyses by neutron-activation methods.

The *X*-ray patterns of the products (Table 2) are free from reflections due to starting materials, alkaline-earth oxides, cuprous oxide, or other known copper(II) compounds. The three compounds are not isostructural, and we were unable to index the patterns satisfactorily, even in the case of $SrCuO_2$ which has been indexed previously (see Table 5).

The magnetic properties of these compounds are summarised in Table 3 and detailed in Table 4. $CaCuO_2$ and $BaCuO_2$ have similar room-temperature magnetic moments, appropriate to octahedrally co-ordinated d^9 systems. $CaCuO_2$ obeys a Curie–Weiss law down to 80 K with a small θ-value. The plot of χ^{-1} *vs.* T for $BaCuO_2$ gives θ = −105 K, suggesting that the compound is ferromagnetic, although at low temperatures the plot deviates above the straight line. There is an increasing field-dependence of the susceptibility at low temperatures which also suggests a ferromagnetic ordering. In contrast, $SrCuO_2$ has a large positive θ and μ_{eff} is well below the spin-only value. These observations suggest an antiferromagnetic ordering, however, no Néel point has been observed down to 80 K.

Of the compounds $A_2Cu_2O_5$ (A = Sc, Y, Bi, or In) only the indium compound has been described previously. All were prepared from the appropriate oxides, the temperatures and times of heating being: 850 °C, 24 h; 850 °C, 40 h; 580 °C, 2 months; and 950 °C, 3 weeks for

TABLE 2

X-Ray powder patterns of alkailne-earth copper oxides

$CaCuO_2$		$SrCuO_2$		$BaCuO_2$		$BaCuO_{2·5}$	
d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{obs}	d_{obs}	I_{obs}
3·14	40	4·09	25	3·36	10	5·71	5
2·75	65	3·53	10	3·24	15	3·72	35
2·51	100	3·49	15	3·15	70	3·66	25
2·43	80	2·99	55	3·05	100	3·50	10
2·274	60	2·83	40	2·98	65	3·47	10
2·023	55	2·73	10	2·90	15	3·23	5
1·933	40	2·61	100	2·64	25	3·20	5
1·609	35	2·41	20	2·59	20	3·09	100
1·570	60	2·31	10	2·50	20	2·85	60
1·496	65	2·237	5	2·33	55	2·66	10
1·410	35	2·042	60	2·257	45	2·63	15
1·372	20	1·954	80	2·161	40	2·60	10
1·301	15	1·812	15	2·131	25	2·25	35
1·273	20	1·786	35	2·103	20	2·191	10
1·227	35	1·766	5	2·080	15	2·148	15
1·710	45	1·749	50	1·977	20	2·125	10
		1·706	10	1·931	25	2·103	10
		1·636	35	1·852	50	2·046	5
		1·519	5	1·811	20	2·017	10
		1·510	35	1·783	40	2·003	5
		1·494	10	1·746	20	1·941	5
		1·413	15	1·585	30	1·934	5
		1·384	10	1·495	20	1·854	5
		1·370	5	1·457	15	1·829	5
		1·344	15	1·314	20	1·687	30
		1·335	10	1·275	20	1·648	5
		1·294	20	1·207	20	1·426	<5
		1·223	5			1·333	5
		1·218	5			1·326	5
		1·707	5			1·320	5
		1·163	5			1·131	5
		1·138	5			1·127	5
		1·135	10			1·122	5
		1·123	5				
		1·117	20				
		1·108	10				
		1·105	5				

TABLE 3

Summary of magnetic data

	μ_{eff}/B.M.				% Field dependence †	
Compound	300 K	80 K	θ/K	Range *	300 K	80 K
$AlCuO_2$	0	0				
$GaCuO_2$	0	0				
$CaCuO_2$	1·72	1·63	10	80	0·1	0·3
$SrCuO_2$	1·42	0·93	500	220	0	0·3
$BaCuO_2$	1·74	2·26	−105	210	2·0	6·0
$Sc_2Cu_2O_5$	1·95	2·07	−35	150	1·6	8·0
$Y_2Cu_2O_5$	1·87	2·22	−45	140	0·5	1·5
$In_2Cu_2O_5$	1·91	2·10	−30	150	3·0	5·0
$Bi_2Cu_2O_5$	1·44	1·01	220	180	0	0
La_2CuO_4	0·69	0·34			0·5	1·2
Al_2CuO_4	1·66	1·25	130	100	0·5	0·8
Ga_2CuO_4	1·80	1·56	45	80	0·6	0·7
$BaCuO_{2·5}$	3·06	2·12	105	200	0·2	0·3
$YCuO_3$	3·01	2·10	220	220	0	0
$LaCuO_3$	3·05	2·18	105	200	0	0

* A Curie–Weiss Law is obeyed above this temperature.
† Difference between susceptibilities measured at 4950 and 6050 Oe.

A = Sc, Y, Bi, and In respectively. All except the indium compound are soluble in hydrochloric acid, the mean oxidation state of the copper in the remaining compounds, determined iodimetrically, is close to II.

The scandium, yttrium, and indium compounds gave diffuse reflectance spectra. The spectra of the scandium and indium compounds consist of single broad peaks, centred at 13 100 and 14 100 cm^{-1} respectively, consistent with their formulation as octahedrally co-ordinated copper(II) compounds. The spectrum of the yttrium compound consists of a broad band centred at 14 100 cm^{-1} with two shoulders, suggesting that the symmetry of the crystal field is lower in this case. These are reflectance spectra from the solids so that no extinction coefficients are available.

TABLE 4

Magnetic susceptibilities of group 2A, 3B, 3A, and bismuth copper oxides as a function of absolute temperature (Measurements at 6050 Oe.)

$CaCuO_2$		$SrCuO_2$		$BaCuO_2$		$BaCuO_{2.5}$	
T	$1/\chi_{Cu}$	T	$1/\chi_{Cu}$	T	$1/\chi_{Cu}$	T	$1/\chi_{Cu}$
308·3	847	299·3	1190	303·4	813	304·8	263
295·0	813	290·0	1176	292·9	781	295·9	256
283·9	781	280·9	1163	284·6	730	287·4	251
274·8	746	272·1	1149	277·1	714	279·3	244
263·2	714	264·6	1136	269·4	671	271·6	241
252·5	694	256·5	1130	262·0	653	263·6	236
240·1	662	245·6	1111	254·2	617	255·6	230
229·0	625	236·0	1087	245·8	575	247·7	224
220·0	610	225·4	1075	237·3	546	239·4	218
209·8	585	215·8	1064	229·6	518	233·5	216
198·2	543	204·9	1041	220·7	490	224·9	212
189·4	526	192·9	1010	211·6	459	216·0	207
178·7	488	182·4	980	202·3	426	206·8	198
166·0	461	169·3	952	192·2	397	197·2	193
155·1	444	154·7	926	179·8	356	187·6	188
146·3	420	136·8	877	166·6	321	177·0	182
135·9	395	120·8	840	155·5	287	165·8	176
124·0	352	103·1	800	143·7	256	154·2	169
115·2	338	90·7	763	130·3	218	142·4	163
104·5	302	78·5	741	116·2	186	130·0	159
96·6	290			98·2	155	117·8	155
87·0	251			80·9	128	104·9	152
78·2	242					92·0	145
						80·1	143

$Sc_2Cu_2O_5$		$Y_2Cu_2O_5$		$YCuO_3$		La_2CuO_4	
T	$1/\chi_{Cu}$	T	$1/\chi_{Cu}$	T	$1/\chi_{Cu}$	T	$1/\chi_{Cu}$
306·8	637	300·9	671	306·2	267	307·2	5076
297·6	621	290·8	662	298·1	264	297·6	5102
289·1	606	281·2	641	287·9	258	289·0	5154
280·9	588	272·0	613	280·3	255	280·0	5154
273·2	565	263·7	592	272·5	249	271·6	5181
265·3	549	256·1	562	263·0	246	263·2	5208
257·3	529	247·4	543	254·1	240	255·0	5235
249·1	510	239·0	523	242·8	235	247·1	5291
240·7	490	230·3	495	232·0	229	237·5	5319
231·9	467	220·5	465	222·6	224	229·2	5376
223·5	446	211·6	444	214·4	220	219·7	5347
214·5	427	201·6	417	205·5	217	209·8	5405
205·1	403	191·5	391	195·2	211	200·5	5435
195·7	382	181·5	364	185·0	209	190·5	5436
185·2	358	169·3	333	177·1	204	179·4	5494
178·3	346	160·8	311	166·3	203	167·4	5435
167·6	315	147·4	279	153·7	196	155·4	5494
155·5	293	133·9	246	143·4	195	142·1	5494
143·8	267	119·8	213	129·1	192	129·0	5586
132·1	241	106·7	183	117·6	188	112·7	5555
119·7	214	91·7	153	107·0	187	96·8	5555
105·8	188	80·9	131	98·2	184	80·1	5618
92·0	164			88·4	183		
78·3	146			78·5	179		

TABLE 4 (*Continued*)

$LaCuO_3$		Al_2CuO_4		Ga_2CuO_4		$In_2Cu_2O_5$	
T	$1/\chi_{Cu}$	T	$1/\chi_{Cu}$	T	$1/\chi_{Cu}$	T	$1/\chi_{Cu}$
307·8	263	306·6	885	315·3	763	309·3	676
298·0	257	295·6	862	302·2	741	296·5	649
288·2	249	286·3	847	293·3	725	286·1	625
279·3	245	278·0	826	284·4	704	276·4	599
270·5	238	270·2	820	276·5	690	267·0	578
262·9	234	262·4	800	267·1	671	258·1	556
254·1	228	254·6	781	258·9	653	249·7	532
241·8	221	246·5	769	250·5	633	239·5	508
232·0	213	238·5	752	242·0	617	230·8	488
222·4	207	230·1	730	233·5	595	220·5	461
214·6	202	221·4	714	224·3	578	210·3	431
205·9	197	212·1	694	215·1	555	200·1	407
195·3	190	202·8	676	205·6	535	189·7	382
185·0	186	193·0	653	196·2	516	179·1	356
177·2	180	183·2	637	186·0	493	169·0	329
166·6	174	172·6	618	174·3	469	158·9	308
153·8	167	161·5	595	162·7	446	149·3	286
142·0	161	150·6	571	151·3	422	139·1	264
130·5	155	139·8	548	139·1	395	127·7	239
118·7	148	128·1	526	127·2	368	116·5	214
109·0	145	115·5	510	117·2	345	107·0	195
98·8	144	102·6	467	106·7	320	97·2	174
87·9	138	91·2	433	97·3	293	87·4	156
78·2	133	82·4	410	87·3	277	79·0	143
				78·7	260		

$Bi_2Cu_2O_5$

T	$1/\chi_{Cu}$	T	$1/\chi_{Cu}$	T	$1/\chi_{Cu}$	T	$1/\chi_{Cu}$
304·4	1163	256·5	1053	206·9	943	140·1	787
296·2	1149	248·0	1041	197·9	926	127·8	757
288·5	1136	239·6	1020	187·3	909	111·7	715
279·6	1111	231·2	1010	176·4	870	96·1	671
272·3	1099	222·7	980	164·8	855	78·0	629
264·7	1075	213·5	961	153·5	826		

The *X*-ray powder pattern of $In_2Cu_2O_5$ is similar to that reported previously.[11] The patterns of the scandium, yttrium, and bismuth analogues (Table 6) showed the absence of impurities and were indexed with orthorhombic unit cells, the dimensions being in Table 5. The *X*-ray pattern of the yttrium compound is rather more complicated than that of its scandium analogue. Attempts to prepare analogous compounds with lanthanum, aluminium, or gallium all gave species A_2CuO_4 while no thallium compounds could be prepared.

The room temperature magnetic moments of $Sc_2Cu_2O_5$, $Y_2Cu_2O_5$, and $In_2Cu_2O_5$ are all close to the value expected for an octahedral d^9 ion (see Tables 3 and 4). They all obey Curie–Weiss laws above *ca.* 140 K with small, negative θ-values. These, together with increasing field-dependence of their susceptibilities at low temperatures, suggest the onset of ferromagnetic ordering. The room temperature moment of $Bi_2Cu_2O_5$ is rather lower: the large positive θ-value (220 K) and absence of field dependence in the susceptibility suggest that this compound is antiferromagnetic although no Néel point has been observed.

The compounds A_2CuO_4 (A = La, Al, or Ga) were prepared by heating equimolar mixtures of the oxides for 24 h at 900, 850, and 1100 °C respectively. La_2CuO_4 is soluble in dilute hydrochloric acid but the other two compounds are insoluble in all mineral acids. The analytical data for all three are consistent with the formulae given, and the presence of copper(II) was confirmed analytically for A = La. The compounds are brown, and give no discrete absorption bands in their electronic spectra.

Above 1100 °C, the aluminium and gallium compounds decompose [9] to A_2O_3 and $ACuO_2$, but when A = La, decomposition does not occur until the temperature exceeds 1200 °C, the products [14] being La_2O_3, Cu_2O, and oxygen.

The *X*-ray powder pattern of La_2CuO_4 is similar [7,8] to that of the K_2NiF_4 structure-type but with a small (*ca.* 0·05 Å) orthorhombic distortion (see Table 5). A similar distortion has been reported for La_2CoO_4 [15] and β-Na_2UO_4.[16] Both Al_2CuO_4 and Ga_2CuO_4 have spinel structures, the cell sizes being listed in Table 5.

TABLE 5

Unit-cell symmetries and dimensions of copper ternary oxides

Compound	Symmetry	*a*/Å	*b*/Å	*c*/Å	Foot-note
$SrCuO_2$	Orthorhombic	12·68	3·91	3·48	*a*
$CuAlO_2$	Hexagonal	2·86		16·95	*b*
	Hexagonal	2·84		16·90	*c*
	Rhombohedral (α = 28° 1′)	5·88			*c*
$CuGaO_2$	Hexagonal	3·01		17·10	*b*
	Hexagonal	3·02		17·09	*c*
	Rhombohedral (α = 29° 4′)	5·95			*c*
$Sc_2Cu_2O_5$	Orthorhombic	18·60	20·05	8·23	*b*
$Y_2Cu_2O_5$	Orthorhombic	15·72	12·76	8·21	*b*
$Bi_2Cu_2O_5$	Orthorhombic	8·57	15·81	6·49	*b*
$In_2Cu_2O_5$	Orthorhombic	24·62	10·54	3·27	*b, d*
La_2CuO_4	Orthorhombic	5·36	5·41	13·25	*b*
	Orthorhombic	5·64	5·41	13·17	*e*
	Orthorhombic	5·0	13·16	5·35	*f*
	Monoclinic (γ = 90° 31′)	3·80	3·80	13·16	*f*
$CuAl_2O_4$	Cubic	8·09			*b, g*
$CuGa_2O_4$	Cubic	8·30			*b, h*
	Cubic	8·39			*i*
$YCuO_3$	Hexagonal	5·31		13·02	*b*
$LaCuO_3$	Hexagonal	5·50		13·22	*b*
	Rhombohedral (α = 60° 51′)	5·43			*j*

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La_2CuO_4 has a very low magnetic susceptibility (Tables 3 and 4) which remains relatively constant over the temperature range 80—300 K. It is not clear why this behaviour occurs, unless there is a very strong antiferromagnetic interaction. Longo and Raccah [7] report a susceptibility less than 1×10^{-6} e.m.u./g for this compound. This is much smaller than we observe but is also attributed to antiferromagnetic exchange. Al_2CuO_4 and Ga_2CuO_4 have more normal room-temperature susceptibilities. Both obey Curie–Weiss laws over most of the range studied, with positive θ-values. Al_2CuO_4 has the lower susceptibility and larger θ-value as might be expected with its smaller unit cell compared with the gallium compound.

(c) *Copper*(III) *Compounds*.—$BaCuO_{2.5}$ was prepared by heating an equimolar mixture of BaO_2 and $Cu(NO_3)_2$ at 580 °C for 24 h in air. The black product is soluble in hydrochloric acid and the mean oxidation state, determined iodimetrically, is III. The *X*-ray powder pattern shows it to be free from starting materials, BaO, CuO, or $BaCuO_2$. We exclude the possibility of a mixture of nickel-(II) and -(IV) for reasons given previously. The magnetic moment is as expected for an octahedrally co-ordinated d^8 ion, *i.e.* Cu^{III}. $BaCuO_2$ changes to $BaCuO_{2.5}$ when heated for 24 h at 600 °C under oxygen at 400 atm. The *X*-ray pattern of this product is the same as that of the material prepared from BaO_2 and $Cu(NO_3)_2$. $BaCuO_{2.5}$ decomposes in air at temperatures above 650 °C.

As we have recently reported,[1] $BaNiO_3$ can be prepared by heating $BaNiO_2$ in oxygen. Similar studies of $BaCuO_2$ using a thermobalance show that oxygen uptake starts at *ca.* 350 °C giving an equilibrium composition $BaCuO_{2.1}$ at that temperature, the composition being derived from both oxygen uptake and chemical analysis. No further oxygen uptake occurs as the temperature is raised and above 600 °C oxygen is again lost. It is thus more difficult to form copper(III) than either nickel-(III) or -(IV). In view of the marked temperature dependence of composition in the $BaNiO_{2.5}$–$BaNiO_3$ composition range, a fresh sample of $BaCuO_2$ was heated at 500 °C under 400 atm of oxygen. The composition of the product was $BaCuO_{2.63}$, the oxygen content being based on the mean oxidation state of the copper, determined analytically. Metal analyses are also given in Table 1, although they are not a sensitive indication of the composition. It thus seems that some copper(IV) can be formed in this compound, as in the corresponding nickel system.

Neither $SrCuO_2$ nor $CaCuO_2$ react with oxygen at atmospheric pressure in the thermobalance. Similarly, we have been unable to prepare $Sr(Ca)CuO_{2.5}$ from the alkaline-earth peroxide and copper(II) nitrate. We are continuing studies of these oxidations at high pressure.

There is some evidence for antiferromagnetism in $BaNiO_{2.5}$ in that θ is positive and the susceptibility deviates upwards from Curie–Weiss low behaviour at low temperatures. However, no Néel point has been observed.

Copper(III) can be stabilised in the phases $YCuO_3$ and $LaCuO_3$. Both were prepared by heating the oxides at 800 °C under 400 atm of oxygen for 40 h. Their *X*-ray powder patterns are similar to that [17] of $LaNiO_3$. The pattern of $YCuO_3$ (see Table 7) was indexed in hexagonal symmetry, the cell dimensions being listed in Table 5. We find that the unit cell of $LaCuO_3$ is also hexagonal whereas it has been reported [5] to be rhombohedral.

Both compounds have room-temperature magnetic moments expected for octahedral d^8 systems, although there is a considerable temperature dependence reflected in the moderately large positive θ-values (Table 3). These, and the shapes of the χ^{-1} *vs.* *T* plots, suggest the presence of an antiferromagnetic interaction which is

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TABLE 6

X-Ray powder patterns of $A_2Cu_2O_5$ (A = Sc, Y, or Bi)

$Sc_2Cu_2O_5$

h	*k*	*l*	$d_{obs.}$	$d_{calc.}$	$I_{obs.}$
1	2	1	6·02	6·02	15
0	0	2	4·11	4·12	10
1	0	2	4·02	4·02	25
0	4	2	3·18	3·18	10
3	5	1	3·12	3·12	25
5	4	0	2·98	2·99	10
2	7	0	2·74	2·75	25
1	7	1	2·67	2·68	65
2	1	3	2·61	2·61	100
1	3	3	2·51	2·51	25
6	0	2	2·48	2·48	10
2	3	3	2·45	2·45	5
3	6	2	2·395	2·393	10
7	3	1	2·368	2·365	
6	3	2	2·322	2·322	10
0	5	3	2·263	2·264	15
2	5	3	2·202	2·200	15
8	2	1	2·185	2·184	
3	9	1	2·030	2·032	5
2	1	4	1·999	1·999	20
9	3	1	1·920	1·920	25
6	7	2	1·871	1·873	20
6	9	0	1·808	1·809	35
4	10	2	1·680	1·680	20
3	11	2	1·610	1·609	
5	11	1	1·604	1·605	15
9	8	0	1·594	1·595	
7	9	2	1·577	1·577	10
4	10	3	1·529	1·529	15
9	9	0	1·515	1·515	25
9	11	0	1·503	1·503	
9	1	4	1·454	1·454	30
5	12	2	1·430	1·429	15
2	10	4	1·419	1·419	10
12	6	0	1·406	1·406	10
7	3	5	1·370	1·370	10
1	1	6	1·365	1·365	
7	9	4	1·314	1·314	5
2	9	5	1·310	1·311	
10	11	0	1·302	1·302	
0	5	6	1·298	1·298	10
11	10	0	1·293	1·292	
10	6	4	1·276	1·276	5

$Y_2Cu_2O_5$

h	*k*	*l*	$d_{obs.}$	$d_{calc.}$	$I_{obs.}$
2	2	0	4·97	4·95	10
0	0	2	4·11	4·10	20
1	2	2	3·37	3·37	25
3	3	0	3·30	3·30	25
1	4	0	3·12	3·12	5
5	0	1	2·94	2·94	30
5	1	1	2·86	2·86	100
1	0	3	2·70	2·70	90
0	1	3	2·68	2·68	60
1	1	3	2·64	2·64	15
4	4	0	2·48	2·48	5
2	4	2	2·40	2·40	10
3	2	3	2·264	2·267	15
7	1	1	2·136	2·135	40
3	3	3	2·106	2·107	5
0	4	3	2·074	2·077	10
6	4	0	2·021	2·024	45
1	2	4	1·937	1·939	10
4	5	2	1·900	1·897	35
8	2	1	1·830	1·830	5
5	6	0	1·762	1·761	20
4	2	4	1·750	1·750	20
6	3	3	1·728	1·729	5
9	1	1	1·693	1·693	5
9	2	1	1·649	1·650	20
2	0	5	1·607	1·607	10
0	5	4	1·600	1·599	
9	3	1	1·586	1·585	15
9	2	2	1·558	1·558	15
10	0	1	1·544	1·544	5
6	5	3	1·521	1·520	35
9	4	1	1·507	1·506	5
8	3	3	1·494	1·494	5
0	8	2	1·485	1·486	
10	0	2	1·466	1·468	15
3	7	3	1·457	1·457	
5	8	0	1·423	1·422	5
2	0	6	1·348	1·348	10
11	1	2	1·342	1·342	
10	5	0	1·338	1·338	10
12	3	0	1·252	1·252	10
8	7	3	1·201	1·201	5
4	4	6	1·198	1·198	
0	1	7	1·168	1·168	5
6	6	5	1·164	1·164	
2	8	5	1·132	1·132	10
8	5	5	1·130	1·130	

$Bi_2Cu_2O_5$

h	*k*	*l*	$d_{obs.}$	$d_{calc.}$	$I_{obs.}$
2	0	0	4·26	4·28	10
0	1	2	3·19	3·18	100
0	2	2	3·01	3·00	10
2	4	0	2·91	2·90	15
0	3	2	2·76	2·763	5
3	2	0	2·689	2·683	30
3	0	1	2·618	2·611	15
1	6	0	2·524	2·518	5
0	6	1	2·441	2·441	5
1	4	2	2·400	2·407	25
3	3	1	2·337	2·340	5
2	3	2	2·325	2·321	10
3	4	0	2·312	2·313	5
3	1	2	2·125	2·123	15
0	2	3	2·090	2·086	5
0	3	3	2·003	2·001	15
0	8	0	1·974	1·976	20
1	3	3	1·943	1·948	45
0	4	3	1·900	1·897	10
2	8	1	1·728	1·729	35
3	1	3	1·715	1·713	10
3	2	3	1·685	1·684	5
2	5	3	1·650	1·648	30
4	0	3	1·523	1·521	20
5	3	2	1·456	1·455	10
2	10	1	1·446	1·445	5
5	4	2	1·414	1·413	25
6	3	0	1·376	1·376	5
1	7	4	1·303	1·302	5
4	0	4	1·293	1·293	15
1	1	5	1·280	1·279	15
6	5	1	1·274	1·275	
5	9	0	1·225	1·226	25
1	4	5	1·221	1·220	
6	2	3	1·177	1·177	15
5	1	4	1·175	1·174	
7	0	2	1·145	1·144	20
7	1	2	1·141	1·141	
1	12	3	1·116	1·116	
1	14	1	1·113	1·112	35
4	0	5	1·110	1·110	
2	10	4	1·095	1·095	20
7	6	1	1·092	1·093	

TABLE 7
X-Ray powder pattern of $YCuO_3$

h	k	l	d_{obs}	d_{cal}	I_{obs}
0	1	2	3·76	3·76	30
1	0	4	2·65	2·657	100
1	1	0		2·656	
0	0	6	2·171	2·170	35
2	0	2		2·169	
0	2	4	1·876	1·878	60
1	1	6	1·683	1·680	25
1	2	2		1·679	
0	1	8	1·534	1·536	55
2	1	4		1·535	
0	3	0		1·533	
3	0	0		1·533	
2	0	8	1·328	1·329	25
2	2	0		1·328	
1	2	8	1·188	1·188	10
1	3	4		1·187	
2	2	6	1·132	1·133	20
4	0	4	1·084	1·084	20

greater for $YCuO_3$ than $LaCuO_3$ as may be expected from the smaller unit cell of the former. Again no Néel points were observed. We find that the susceptibility of our preparation of $LaCuO_3$ is some ten times greater than that previously reported [5] and θ is much smaller (105 K *cf.* 650 K). A similar discrepancy occurs between our measurements [1] on $LaNiO_3$ and those of Hagenmuller. The source of these discrepancies is not clear. Our measurements were reproducible and are also similar to those on $YCuO_3$, and analyses and oxidation state determinations confirm the presence of copper(III).

EXPERIMENTAL

Preparative Procedures.—The starting materials and duration and temperature of heating are given in the text. In all cases, stoicheiometric proportions of reactants were accurately weighed, finely ground, and thoroughly mixed. Apart from the reactions at high pressure, mixtures were periodically removed from the furnace, reground, and returned to the furnace. High-pressure reactions were carried out in partially closed platinum containers in steel pressure vessels.

Analyses.—Ga_2CuO_4 and $GaCuO_2$ could not be dissolved and were analysed by neutron-activation methods. Al_2CuO_4 and $In_2Cu_2O_5$ were fused in NaOH in order to get them into solution.

Copper was determined iodimetrically. Calcium, strontium, and barium were analysed after removal of copper as the sulphide: barium, gravimetrically as the sulphate, strontium by titration with EDTA at pH = 12, and calcium by precipitation as the oxalate followed either by ignition to the oxide or titration of the oxalate. The remaining compounds were analysed by determining the total metal by back-titration of excess of EDTA with standard zinc sulphate, and the copper iodimetrically.

X-Ray diffraction patterns were obtained from a Phillips recording diffractometer using quartz or potassium chloride as internal standards. Magnetic suceptibilities were measured by the Gouy method using conventional apparatus calibrated against nickel chloride solution. The Curie–Weiss law was used in the form $\chi = \frac{C}{T + \theta}$ and all values of magnetic moments were calculated from the relationship $\mu_{eff} = 2{\cdot}828(\chi_A{\cdot}T)^{\frac{1}{2}}$ B.M. Diffuse reflectance spectra were recorded with a Beckman DK2-A spectrometer and the thermobalance was a Stanton–Redcroft model MF-H5 instrument.

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