Study of the Oxides of Copper Formed in Air

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Oxides of copper formed in air at temperatures between 150°C and 1030°C, and for times of formation up to one hour have been studied. Their composition, structure by electron reflection and rectification — all these as a function of the thickness of the film — have been investigated. At first small crystallites of Cu_2O are formed, then they increase in size and get oriented. These crystallites of Cu_2O gradually change over to those of CuO showing a three ring pattern, definite orientation and finally a fibrous structure. At high temperatures and appreciable times of formation a layer of Cu_2O is formed below the CuO layer. Rectification of CuO films showing orientation and of the composite film $Cu_2O + CuO$ has been studied in detail. A plausible mechanism for the formation of the various oxides is suggested. The following special points have been observed: (1) Cu_2O changes into CuO, crystallite by crystallite, (2) The three ring pattern is due to oriented monoclinic CuO, (3) CuO oriented shows a small rectification in a direction opposite to that of Cu_2O, (4) At high temperatures, when a change of orientation of CuO can occur, a Cu_2O film is formed below the CuO film, (5) The composite layer $Cu_2O + CuO$ shows a rectification comparable with Cu_2O but with a higher voltage response.

Oxides of copper formed in air or oxygen have been studied by Thomson[1], Murison[2], Preston and Bircumshaw[3], Miyake[4], Bound and Richards[5], Honjo[6], and Blankenburg[7]. The general observation appears to be that Cu_2O (cuprite) is formed at temperatures up to 200°C in air or oxygen, whereas at temperatures above 600°C, CuO (tenorite) is formed. At intermediate temperatures i. e. roughly between 300°C and 500°C a new type of oxide CuO′ is formed. This is generally regarded as a mixture of Cu_2O and CuO, but Honjo suggested that it is an oriented form of CuO. This substance CuO′, when studied by the method of electron reflection, shows three characteristic rings called the 'three ring pattern'.

We have studied oxides of copper formed on polished copper blocks in air at temperatures between 150°C and 1030°C. At each temperature the time for which the block was heated was changed. The oxides so formed were investigated by the method of electron reflection. In addition we have studied the electrical properties of these layers, their rectification if any, their thickness, as well as the change in the composition of the oxide layers and their properties as a function of the thickness of the layers.

We find that the nature of the oxide film formed depends on the pressure, the temperature, and the time. It also depends to some extent on the nature of the substrate. In this paper we are reporting the work done at atmospheric pressure*. We observe that in general at low temperatures a thin film of Cu_2O is formed which becomes oriented if the time of formation is long enough. As the temperature and the time of formation increase Cu_2O gradually changes over into CuO, producing an oriented film of CuO. If the temperature and the time are increased still further we get a Cu_2O film formed below a CuO film. This is easily noticed by the composite film showing a considerable rectification, and the surface an absence of orientation of the outside CuO film. The rectification of this composite film of $Cu_2O + CuO$ is also investigated. A remarkable observation is the small rectification** shown by a CuO film alone, but in a direction opposite to that of Cu_2O.

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[1] G. P. Thomson, Proc. Roy. Soc., (A) **128**, 649 [1930].

[2] C. A. Murison, Phil. Mag. **17**, 96 [1934].

[3] G. D. Preston and L. L. Bircumshaw, Phil. Mag. **20**, 706 [1936].

[4] S. Miyake, Sci. papers Inst. Phys. Chem. Res. Tokyo, **29**, 167 [1936].

[5] M. Bound and D. A. Richards, Proc. Phys. Soc. (Lond.) **51**, 257 [1939].

[6] G. Honjo, J. Phys. Soc. (Japan) **4**, 330 [1949].

[7] G. Blankenburg, Ann. Phys. **14**, 308 [1954].

* The study of oxides formed at other pressures has been completed and will be reported separately.

** This rectification of CuO is also being investigated and a detailed report will be soon published.

Experimental (General)

In the beginning we were guided by a remark of Murison[2], "if air or oxygen are blown through the furnace tube during the heating (300° C—500° C) of the copper block, the oxide so formed exhibits the three ring pattern with electron reflection".

Our copper blocks were polished on 0/0 to 0/4 emery papers under liquid paraffin, so as to prevent the formation of a thin oxide layer. The blocks were then thoroughly cleaned and heated at a predetermined temperature for one minute, when hot air was flowing through the furnace tube. The results of these observations are given in Table 1. While doing these experiments we found that it is rather difficult to maintain the temperature exactly constant when hot air is flowing through the furnace tube. This effect became noticable with our thermocouple at temperatures beyond 800° C. We therefore decided to work in still air. We found that the same effects, as in Table 1, are observed at corresponding temperatures in still air, if the time of heating is 2 minutes instead of 1 minute. All our subsequent observations were now carried out in still air.

These observations are summarised in Fig. 1. We have worked in the range 150° C to 1030° C and normally heated the blocks for ½, 1, 5, 10, 15, 30 and 60 minutes. Additional points were investigated as and when required. The specimens so formed were studied by the method of electron reflection. Our observations showed the following interesting results.

a) At low temperatures and for short times of heating a thin layer of Cu_2O is formed. This layer shows a few diffuse rings of a typical face centred cubic configuration, viz $\sqrt{3}$, $\sqrt{4}$, $\sqrt{8}$, $\sqrt{11}$ $\sqrt{12}$, $\sqrt{19}$ $\sqrt{20}$. The corresponding cell size is 4.3 ± 0.1 Å, which compares favourably with 4.26 Å, the cell size of a Cu_2O cell. As the time for which the block is heated and or the temperature at which it is heated increases there is a tendency to form sharper rings. Now in addition to the rings mentioned above $\sqrt{2}$, $\sqrt{6}$, $\sqrt{18}$ rings of Cu_2O appear. These

Temp. °C	Resistance in ohms R_1	R_2	R_1/R_2	Diffraction pattern
200± 5	less than one		—	Broad rings of Cu_2O
275± 5			—	Cu_2O (S.M.) + CuO (S.F.)
325± 5			—	Cu_2O (S.M.) + CuO (S.F.)
375± 5	1	1	1	Cu_2O (S.F.) + CuO (S.M.)
410± 5	1	1	1	Three ring pattern
460± 5	10	10	1	Visible orientation of CuO
620± 10	15	20	1.3*	
700± 10	17	25	1.4*	
750± 10	25	30	1.2*	
850± 10	300	100	3**	CuO non-oriented
950± 10	1650	550	3**	

Resistances are measured at 2 Volts.

* Indicates direction of rectification opposite to that of Cu_2O rectifier.
** Indicates usual direction of Cu_2O rectifier.

First letters: S — Sharp; M — Medium; B — Broad.
Second letters: F — Faint; M — Medium; I — Intense.

These indicate the nature and intensity of the rings respectively.

Tab. 1. Hot air flowing over polished copper blocks for *one* minute.

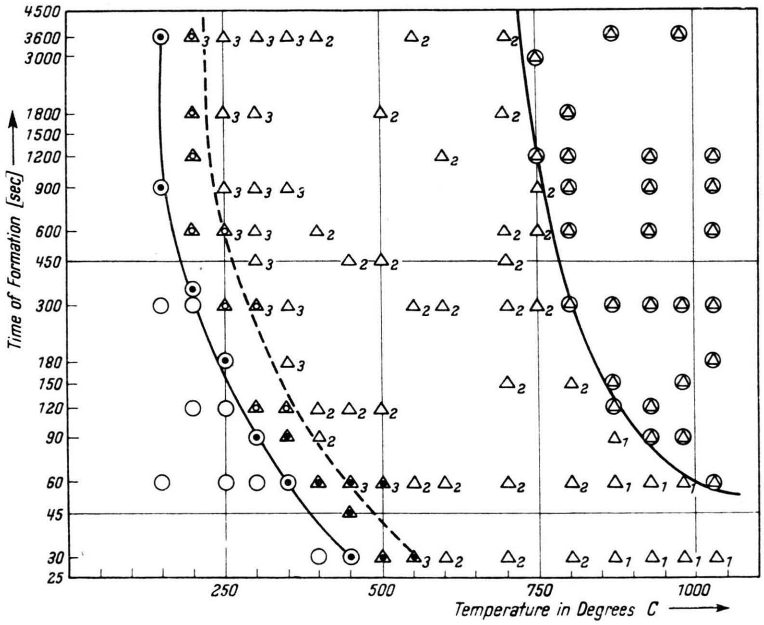

Fig. 1. In the figure the Δ's represent CuO. The subscript 3 indicates the three ring pattern. The subscript 2 indicates the same structure as that of the specimen showing a three ring pattern but with a still larger number of crystallites oriented. For both Δ_3 and Δ_2 the crystallites of CuO are so oriented that the diagonal planes (110 and 011) are parallel to the substrate. The subscript 1 indicates that a larger number of crystallites of CuO are now so oriented that the side faces (010, 001 and 100) of the monoclinic cell are parallel to the substrate.

A circle represents Cu_2O. A dot inside the circle indicates an orientation of Cu_2O crystallites with the diagonal planes (110) parallel to the substrate. A Δ inside a circle indicates the presence of CuO and Cu_2O, but the Cu_2O layer is below the CuO layer. A circle inside the Δ indicates the simultaneous presence of Cu_2O and CuO crystallites side by side. If the circle inside the Δ is hollow, Cu_2O is nonoriented; whereas a black circle indicates its orientation.

rings a little later begin to show (110) orientation; indicating that in a large number of crystallites the diagonal planes of the Cu_2O cell are parallel to the substrate.

b) With a further increase of time and temperature CuO rings also begin to appear side by side with the Cu_2O rings. At first only the prominent rings (2.54, 1.63 and 1.41 Å) of normal CuO are seen, and then the three ring pattern of Murison begins to show itself (Table 2). As the time and temperature are further increased Cu_2O rings disappear and the three ring pattern alone is seen (Fig. 2*). At a little higher temperature the three ring pattern begins to show clear signs of orientation (Fig. 3). At times the orientation is so marked, that the pattern seen, in the X-ray language is a fibrous pattern (Fig. 4). This pattern is due to a large number of crystallites of CuO being so orientated that the diagonal planes of the monoclinic CuO cell (110 and 011) are parallel to the substrate (Table 3, A).

c) At a temperature of 800°C we found that the film formed in 2½ minutes is showing a typical fibrous three ring orientation but a film formed in 5, 10, 15 or 30 minutes shows normal rings of unoriented CuO powder. A similar result was also observed[8] at 1030°C. Here a film formed in ½ minute shows the typical fibrous orientation, whereas films formed in 1, 5, 10 and 15 minutes show unorientated rings of CuO powder. Later detailed ivestigations (given below) showed that this change of the surface structure is due to the formation of a Cu_2O film below the CuO film. From the graph it will be seen that this formation of a Cu_2O film below the CuO film occurs at all temperatures above 750°C. In this connection it is worth noticing that at temperatures beyond 800°C, when the film is heated only for a short time, we get a layer of pure CuO, but this layer shows an orientation of the CuO crystallites with the side faces (010, 001 and 100) parallel to the substrate (Table 3, B). This orientation of CuO differs from the one observed at lower temperatures. Such a change of orientation with temperature is not unexpected[9].

d) From the graph it appears that there is a line of demarkation (rather broad) which separates the oriented CuO from the non-oriented CuO. There is also a broad band which separates Cu_2O from the three ring pattern. In this band both

Δ	Δ_3	$\overline{\Delta}_3$	Cu_2O	CuO powder	Three ring pattern
—	W. 3.08	S.* 2.98	3.02 ($\sqrt{2}$)	—	—
—	W. 2.78	S. 2.78	—	—	V. S. 2.73
S. 2.5 ± .04	V. S. 2.5 ± .04	V. S. 2.5 ± .04	2.47 ($\sqrt{3}$)	S. 2.54	V. S. 2.54
S. 2.34	V. S. 2.35	V. S. 2.35	—	S. 2.35	V. S. 2.34
W. 2.16	S. 2.10	W.** 2.16	2.13 ($\sqrt{4}$)	—	—
S. 1.90	S. 1.92	S. 1.88	—	W. 1.85	S. 1.88
V. W. 1.76	W. 1.76	W. 1.76	—	W. 1.73	V. W. 1.73
—	V. W. 1.61	V. W. 1.6	—	S. 1.63	W. 1.63
S. 1.54	V. S. 1.54	S.* 1.52	1.51 ($\sqrt{8}$)	S. 1.54	—
S. 1.39	V. S. 1.42	S. 1.42	—	V. S. 1.41	V. S. 1.41
S. 1.31	V. S. 1.31	S.** 1.33	1.28 ($\sqrt{11}$)	W. 1.33	S. 1.31
			($\sqrt{12}$)		
W. 1.2	V. W. 1.20	W. 1.20	—	W. 1.18	S. 1.17
V. W. 1.11	V. W. 1.13	W. 1.11	—	W. 1.11	S. 1.08
—	—	S.* 1.01	1.01 ($\sqrt{18}$)	—	W. 1.03
—	W. 0.975	W. 0.985	0.975 ($\sqrt{19}$)	—	—
			($\sqrt{20}$)	—	—
—	—	W. 0.89	0.875 ($\sqrt{24}$)	—	S. 0.88
—	—	W. 0.745	0.755 ($\sqrt{32}$)	—	—

Δ mixture of non-oriented oxides ($CuO + Cu_2O$).
Δ_3 mixture of oriented CuO and non-oriented Cu_2O.
$\overline{\Delta}_3$ mixture of oriented CuO and oriented Cu_2O.
* Indicates arc at the centre. ** Indicates arc at about 40° from the centre.

Tab. 2. The '*d*' values for all rings in the case of mixtures in Å.

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* Fig. 2, 3, 4 on p. 160 a.

[8] J. Bardeen, W. H. Brattain and W. Shockley, J. Chem. Phys. **14**, 714 [1946].

[9] K. R. Dixit, Phil. Mag. **16**, 1049 [1933].

A Δ_2					B Δ_1			
'd' spacing observed in Å	corresponding indices	Angle measured in deg.	Angle calculated for		Angle in deg. measured	Angle calculated for		
			110 planes	011 planes		010 planes	100 planes	001 planes
2.73	110	0	0	48	Q	37	52	90
2.53	111 002	25,85	26 90	26 54	P	42 90	56 90	60 0
2.34	$\bar{1}11$ 200	35	76 52	36 90	P	47 90	115 0	62 90
1.98	112	40	44	23	R	—	—	—
1.88	202	45	61	66	Q	90	34	41
1.73	$\bar{1}12$	35	80	37	R	—	—	—
1.68	003 020	45	90 36	54 30	0	90 0	90 90	0 90
1.54	113	30	57	30	Q	64	70	23
1.41	022	0	48	0	80,30	34	90	56
1.385	220	0	0	48	80,30	37	52	90
1.31	$\bar{3}11$ 312	P	102 42	63 53	70	67 67	145 28	75 75
1.27	004 222 303	P	90 26 61	54 26 65	0,35	90 42 90	90 56 34	0 60 41
1.16	$\bar{2}22$ 400	35	76 90	36 54	0,45	47 90	115 0	62 90
1.08	131	35	27	26	70	17	76	78
0.96	033	50	48	0	45	34	90	56
0.94	404	55	67	65	Q	90	34	41
0.915	330	0	0	48	Q	37	52	90
0.88	$\bar{3}31$	40	73	43	40	39	126	80
0.855	006 333	55	26 90	27 57	0,60	90 42	90 56	0 60
0.77	$\bar{3}33$ 600	50	76 52	56 36	0,50	47 90	115 0	62 90
0.72	044	0	48	0	Q	34	90	56
0.705	505	R	61	65	Q	90	34	41
0.69	440	0	0	48	Q	37	52	90

P — Ring uniform in intensity. Q — Intensity of the ring not uniform; a small varation is observed. R — Ring extremely faint.
Calculated values of the angles are given to the nearest degrees.

Tab. 3. Comparison of observed and calculated angles of orientation.

Cu_2O and CuO are present. The nature of each of them in the mixture is in general similar to their nature in the pure state in the neighbourhood. In three cases the crystallites of both CuO and Cu_2O are oriented (Table 2, columns 3, 4 and 6).

Experimental (Double layer)

We have already described the peculiar changes observed in the structure of the surface CuO at temperatures above 750° C. As the oxides of copper formed at these high temperatures show rectification, the first property we decided to investigate was the rectification of these films. But in order to get a clear idea of the changes produced at 750° C, we also measured the rectification of the films formed at 700° C. We found that the films of CuO which showed orientation, showed a small rectification in a direction opposite to that of Cu_2O, whereas the films which showed the presence of unoriented CuO at the surface, gave a very significant rectification but now in the same direction as that of Cu_2O. This led us to suspect that a film of Cu_2O must have been formed; but as the surface structure was still that of CuO, we were left wondering whether this film of Cu_2O has been formed below the surface CuO film.

This matter was investigated by finding out the surface structure and rectification of the film at various depths. The surface structure of the film as formed and its rectification were determined. The film was then rubbed on 0/2 emery paper under liquid paraffin. This removed some part of the film. The amount of portion removed was ascer-

	Obs. No.	Total oxide removed in mgms.	Colour	Diffraction pattern	Resistance in ohms.		R_1/R_2
					R_1	R_2	
(a)	1	0	Black	CuO *(unoriented)*	13000	4400	2.9
	2	0.65	Black	CuO *(unoriented)*	2675	175	15.4
	3	3.25	Blackish red	CuO *(unoriented)*	2625	125	21
	4	5.35	Red	Cu_2O	2400	100	24
	5	8.60	Red	Cu_2O	2400	90	26.6
	6	14.6	Red	Cu_2O	2000	90	22.2
	7	15.75	Red	Cu_2O	800	60	13.3
	8	17.75	Red	Cu_2O	600	60	10
	9	20.75	Red	Cu_2O	400	50	8
	10	21.95	Red	Cu_2O	—	Shorted	—
	11	36.0	Copper colour	No pattern	—	Shorted	—
(b)	1	0	Black	CuO (oriented)	1000	500	2*
	2	0.65	Black	CuO *(unoriented)* **	300	140	2.1*
	3	5.60	Black	— do —	100	50	2*
	4	17.3	Black	— do —	30	30	1
	5	27.3	Copper colour	faint rings of copper	—	—	—

Resistances are measured at 2 Volts.

(a) Oxide formed at 1030° C for 2.5 min. (b) Oxide formed at 700° C for 30 min.

* denotes rectification in the direction opposite to that of Cu_2O.

** The orientation of the surface layer is probably lost during the process of rubbing.

Tab. 4. Shows the variation of the properties of the oxides formed as a function of the depth from the free surface.

tained by a change in weight. The surface structure of this new surface and the corresponding rectification was determined. This process was continued till we reached the mother copper block. The necessary details in two typical cases are shown in Table 4.

These results clearly show that at a temperature of 750°C and above a Cu_2O film begins to form below a CuO film. The Cu_2O film acts like a normal rectifier, and the rectification of Cu_2O being greater than that of CuO predominates. The rectification of the composite block is therefore in the same direction as that of Cu_2O. The numerical value of the rectification of the composite block is comparable with that of Cu_2O, but its voltage response is appreciably different (Fig. 5). It will be seen that the maximum rectification occurs in this case between 10 to 15 volts compared with 4 to 6 volts in the case of normal Cu_2O rectifiers. Further the heating effect begins to play a dominant rôle at about 25 volts in this case, compared with 10 volts in the case of Cu_2O.

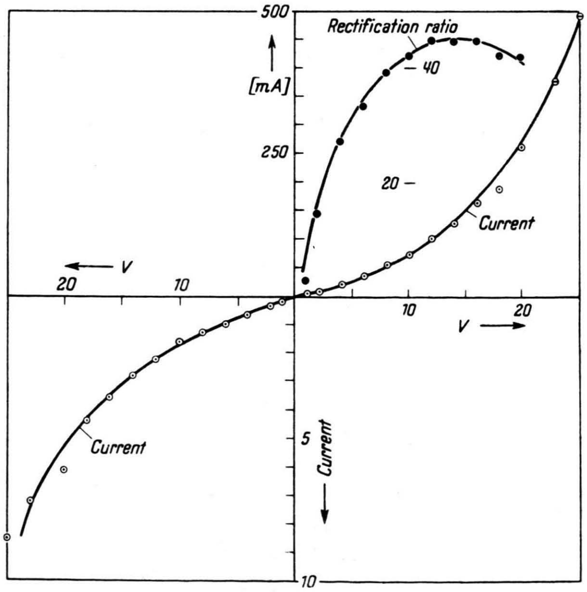

Fig. 5. Current voltage and rectification ratio for the composite film $Cu_2O + CuO$. At 23 volts and 25 volts the heating effect begins to show itself. This is shown by a line inside the circle.

The study of the variation of the structure with thickness at various temperatures (Table 5 and Fig. 6) indicates that the thickness of the CuO film at the surface remains appreciably constant, whereas the thickness of the underlying Cu_2O film increases with the temperature and the time of formation according to well established principles[10].

Time in minutes	700° C				800° C				930° C				1030° C			
	Amount in mgm.			Nature of surface layer	Amount in mgm.			Nature of surface layer	Amount in mgm.			Nature of surface layer	Amount in mgm.			Nature of surface layer
	CuO	Cu_2O	Total		CuO	Cu_2O	Total		CuO	Cu_2O	Total		CuO	Cu_2O	Total	
0.5													7.7	—	7.7	Δ_1
1	3.75	—	3.75	Δ_2	4.1	—	4.1	Δ_2	6.35	—	6.35	Δ_1	7.4	13.95	21.35	Δ
1.5									10.45	—	10.45	Δ_1				
2									5.5	12.2	17.7	Δ				
2.5	6.1	—	6.1	Δ_2	8.4	—	8.4	Δ_2								
3													5.85	55.0	60.85	Δ
5	10.95	—	10.95	Δ_2	5.425	7.425	12.85	Δ	5.1	26.55	31.65	Δ	5.6	73.9	79.5	Δ
7.5					5.71	16.44	22.15	Δ								
10	14.97	—	14.97	Δ_2	5.0	31.65	36.65	Δ	5.25	45.6	50.85	Δ	7.1	111.0	118.1	Δ
15	17.82	—	17.82	Δ_2	6.4	42.6	49.0	Δ	6.1	74.04	80.14	Δ	6.9	125	131.9	Δ
20	21.60	—	21.60	Δ_2	5.65	57.0	62.65	Δ	4.9	90.41	95.31	Δ	7.6	138	145.6	Δ
30	27.3	—	27.3	Δ_2	5.7	88.7	94.4	Δ								

Δ_1 and Δ_2 CuO oriented; Δ CuO non-oriented.

Tab. 5. Shows how the surface films grow as a function of the temperature and time.

Experimental (The Three Ring Pattern)

The nature of the oxides was studied by electron reflection. A cold cathode camera, coupled with magnetic focussing between the anode and the crystal, was used. We worked at voltages in the neighbourhood of 30 KV. The times of exposures in all cases were fractions of a second.

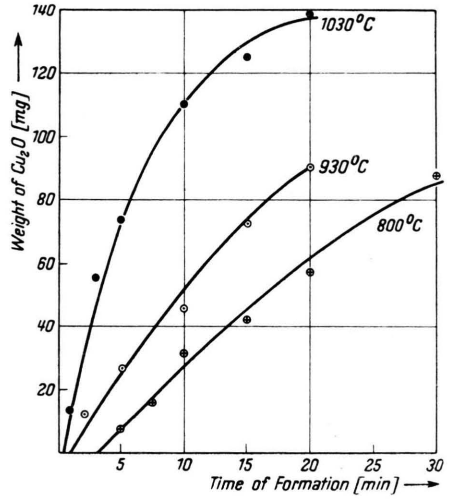

Fig. 6. Shows the increase in the thickness of the Cu_2O film formed below the CuO film, as a function of time and temperature.

The three ring pattern (Fig. 2) is characterised by the appearance of the first three rings of almost equal intensity. Table 6 gives the *d* values of all the rings observed for this pattern by us together with the observed spacing with CuO powder impregnated on a polished lead block. The table also gives the calculated spacings for all allowed rings of tenorite and the *d* values of Murison for the three ring pattern. It will be seen that the three ring pattern does not show any forbidden ring of tenorite and the corresponding *d* values are also favourably comparable.

The first prominent ring in the three ring pattern $d = 2.73$ Å is a permissible ring of the CuO monoclinic lattice but does not correspond to any permitted ring of the Cu_2O cubic lattice (face and body centred interpenetrating). It does not, therefore, appear possible to explain this ring as due to the simultaneous presence of the crystallites of CuO and Cu_2O. When these crystallites are present side by side, we observed the prominent rings of both of them and even their simultaneous orientations (Table 2). But when a layer of CuO crystallites is placed above a similar layer of Cu_2O, we get normal rings of unoriented CuO powder. It is, therefore, unlikely that the three ring pattern is produced by a mixture of the crystallites of Cu_2O and CuO.

The assumption that this pattern is due to some unknown oxide CuO′ of copper, appears to be uncalled for, specially as the three ring pattern does not contain any forbidden rings of tenorite. We shall, therefore, assume with Honjo[6] that this pattern is due to the oriented crystallites of CuO and proceed to describe the evidence we have been able to collect in this behalf.

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[10] N. Cabrera and N. F. Mott, Rep. Progr. Phys. Vol. XII, 163 (London 1949).

From Fig. 1 it will be seen that the Cu_2O crystallites which are formed at low temperatures gradually change over to crystallites showing a three ring pattern (Δ_3). This structure, when once formed at a particular temperature, does not change even when there is a tenfold increase in time for which it is heated. At a higher temperature the only change that is observed is that we see a Δ_2 pattern (Fig. 3) or a visibly orientated Δ_3 pattern (Table 6). Or the effect of the additional time for which the oxygen is allowed to combine with the free surface is to keep the nature of the surface unaltered. This probably indicates that the surface layer contains crystallites which are already saturated with oxygen i. e. it contains CuO crystallites. Table 6 shows that the *d* values are identical for the Δ_2 and the Δ_3 patterns, the only difference being the degree of orientation or the number of oriented crystallites. The three ring pattern Δ_3 is thus really a Δ_2 pattern but orientated to a much smaller extent. The observed orientations for Δ_2 are those produced by the diagonal planes (110 and 011) of tenorite being parallel to the substrate. In the present work we have succeeded in obtaining clear definite pictures of CuO crystallites showing orientations and we are not compelled to assume (like Honjo), only the redistribution of intensities (Δ_3 pattern) as its evidence.

We also deposited a copper film (~2000 Å) on a polished copper block, glass plate and polished silver block. The copper films were simultaneously

Murison	Observed values for		Calculated values for CuO; monoclinic		CuO powder on lead block
	Δ_3	Δ_2	*d*	*h k l*	
V. S. 2.7	V. S. 2.73	V. S. 2.73 (α)	2.757	1 1 0	—
V. S. 2.49	V. S. 2.54	V. S. 2.53 (β)	2.558 2.526	0 0 2 1 1 1	S. 2.54
V. S. 2.26	V. S. 2.34	V. S. 2.34 (γ)	2.335 2.331	$\bar{1}$ 1 1 2 0 0	S. 2.35
—	V. W. 1.95	V. W. 1.98 (δ)	1.979	1 1 2	—
S. 1.88	S. 1.85	S. 1.88 (δ)	1.891	2 0 2	W. 1.85
W. 1.74	W. 1.73	W. 1.73 (γ)	1.792	$\bar{1}$ 1 2	W. 1.73
—	—	S. 1.68 (δ)	1.681 1.698	0 0 3 0 2 0	—
W. 1.59	W. 1.6	—	1.615 1.596	0 2 1 $\bar{2}$ 0 2	S. 1.63
—	W. 1.54	W. 1.54 (γ)	1.521	1 1 3	S. 1.54
—	V. S. 1.41	V. S. 1.41 (α)	1.415	0 2 2	V. S. 1.41
V. S. 1.39	V. S. 1.385	V. S. 1.385 (α)	1.374	2 2 0	—
S. 1.29	S. 1.31	S. 1.31	1.324 1.314	3 1 2 $\bar{3}$ 1 1	W. 1.33
W. 1.26	W. 1,27	W. 1.27	1.26 1.28	303; 222 0 0 4	W. 1.25
S. 1.15	S. 1.16	S. 1.16 (γ)	1.159 1.163	$\bar{2}$ 2 2 4 0 0	W. 1.18
—	S. 1.12	—	1.12	$\bar{1}$ 1 4	W. 1.11
S. 1.08	S. 1.08	W. 1.08 (γ)	1.09	1 3 1	—
—	W. 0.96	S. 0.96 (δ)	0.9590 0.9524	$\bar{1}$ 2 4 0 3 3	—
S. 0.943	S. 0.94	S. 0.94 (δ)	0.9434	4 0 4	—
W. 0.909	W. 0.915	S. 0.915 (α)	0.9174	3 3 0	—
—	—	W. 0.895	0.9025	4 1 4	—
S. 0.877	S. 0.88	W. 0.88 (δ)	0.885	$\bar{3}$ 3 1	—
S. 0.842	S. 0.855	S. 0.855 (δ)	0.8547 0.8475	0 0 6 3 3 3	—
—	W. 0.77	W. 0.77 (δ)	0.777 0.7752	$\bar{3}$ 3 3 6 0 0	—
S. 0.717	S. 0.72	S. 0.72 (α)	0.717	0 4 4	—
—	—	W. 0.705 (δ)	0.7092	5 0 5	—
S. 0.696	S. 0.695	S. 0.69 (α)	0.69	4 4 0	—

α, β, γ and δ indicate positions of arcs at different angles from the centre $\alpha = 0°$; $\beta = 25°$; $\gamma = 30°—40°$ and $\delta = 40°—60°$.

Tab. 6. Gives the observed and calculated values of the '*d*' spacings for the three ring pattern in Å.

evaporated in vacuum on the three substrates. In addition we also evaporated on five glass plates films of a thickness of about 500, 1000, 3000, 6000 and 7500 Å. All these specimens together with one polished copper block, in all nine specimens, were heated in air for 2 minutes at 500°C. Electron reflection pictures were taken with all these surfaces, and also with a polished lead block on which CuO powder is impregnated. Table 7 gives the d values and the corresponding intensities for all the rings. Oxide film on polished copper block shows the Δ_2 pattern. The film deposited on the copper block and subsequently oxidised shows the Δ_3 pattern. A similar film on the silver block shows unoriented CuO powder pattern. The films on all the glass blocks, for all the thicknesses show mainly rings of unoriented CuO, but with traces of orientation. These observations also indicate that the free surface in all these cases, formed at 500°C (the temperature favourable for the formation of the three ring pattern specimen) are composed of crystallites of tenorite (CuO).

Calculated	Polished copper block oxidised	Evaporated film of copper on			CuO powder impregnated on polished lead block
		Copper block and oxidised	Glass plate and oxidised	Silver block and oxidised	
2.757	V. S. 2.73 (α)	V. S. 2.7	S. 2.74	—	—
2.558 2.526	V. S. 2.53 (β)	V. S. 2.52	S. 2.5	S. 2.53	S. 2.54
2.335 2.331	V. S. 2.34 (γ)	V. S. 2.28	—	S. 2.34	S. 2.35
1.979	V. W. 1.98	—	W. 1.95	—	—
1.891	S. 1.88 (δ)	S. 1.86	W. 1.84	W. 1.85	W. 1.85
1.79	W. 1.73 (γ)	W. 1.75	—	W. 1.75	W. 1.73
1.68	S. 1.68 (δ)	—	—	—	—
1.615 1.596	W. 1.6	W. 1.6	—	S. 1.63	S. 1.63
1.521	W. 1.54 (γ)	W. 1.5	W. 1.54	W. 1.52	S. 1.54
1.415	V. S. 1.41 (α)	—	V. S. 1.44	V. S. 1.41	V. S. 1.41
1.374	V. S. 1.385 (α)	V. S. 1.37	—	—	—
1.324 1.314	S. 1.32	S. 1.34	W. 1.32	W. 1.31	W. 1.33
1.28	W. 1.27	S. 1.26	W. 1.28	W. 1.25	W. 1.25
1.16	S. 1.16 (γ)	W. 1.16	W. 1.15	W. 1.18	W. 1.18
1.12	—	S. 1.12	—	—	W. 1.11
1.09	W. 1.08 (γ)	—	W. 1.07	—	—
0.9590 0.9524	S. 0.96 (δ)	S. 0.96	S. 0.95	—	—
0.9434	S. 0.94 (δ)	—	—	—	—
0.92	S. 0.925	S. 0.925	—	—	—

α, β, γ and δ have the same significance as in Table 6.

Tab. 7. Shows the values of 'd' spacings for oxide films formed on different substrates in Å.

Mechanism of the formation of the oxide layers

In the light of the experimental evidence obtained we should like to put forward the following suggestions about the manner in which the various oxide layers are formed.

At low temperatures and for limited periods of heating small crystallites of Cu_2O are formed. The mechanism of formation is probably that given by Mott[10], wherein the copper ions migrate and the oxygen ions diffuse to occupy the vacancies created by the migration of the copper ions. As the temperature and or the time increase, the size of these Cu_2O crystallites increases and sharp rings of Cu_2O are seen. With a further increase in time and temperature Cu_2O rings show that at least some of the crystallites become oriented with the diagonal face (110) parallel to the substrate. With a further increase in the time of heating it is possible for some oxygen atoms to go into solid solution[7] in the Cu_2O crystallites, at first expanding the Cu_2O lattice which quickly changes over into a CuO lattice, keeping the planes of orientation (if any) unaltered during the change, giving rise to the (110 or 011) orientation of CuO.

A simultaneous presence of the crystallites of Cu_2O and CuO is indicated by the prominent rings of both the lattices appearing simultaneously. The relative intensities of these two oxides show a gradual and progressive change with time and temperature. The intensity of Cu_2O rings diminishes and that of CuO increases. It is worth noting that we have observed three cases, showing simultaneously equally intense rings of oriented Cu_2O and CuO. These observations clearly show the simultaneous presence of the two varieties of crystallites (Cu_2O and CuO) which later on change into one variety (CuO). The above experimental evidence leads us to suggest, that the change from one variety (Cu_2O) to the other (CuO) is taking place crystallite by crystallite.

With a further increase in temperature and time only CuO crystallites are seen to be present, either in the Δ_3-form or in the dominently oriented Δ_2-form. This orientation (110 or 011), at a temperature of 870°C changes over into a (010) or a Δ_1-orientation. The change of orientation on a given base as a function of the temperature is a well known process[9]. Although the visual indication of this change is observed at 870°C it is quite possible to expect a little instability, due to a tendency on the part of atoms to rearrange themselves, even at lower temperatures in the neighbourhood of 870°C. This instability is actually observed at 750°C and beyond. At these temperatures we have a clear evidence of the formation of a Cu_2O layer below the surface CuO layer. We are suggesting that the formation of this double layer is due to the instability of the CuO crystallites arising out of a tendency on the part of the atoms concerned to change the orientation.

Table 5 and Fig. 6, which show the thicknesses of the Cu_2O and the CuO films, clearly bring out the fact that the thickness of the CuO film remains fairly constant but the thickness of the Cu_2O film formed below it increases as a function (approximately parabolic) of the temperature and the time. This variation of the thickness of Cu_2O is in conformity with the theory of Mott[10] and Cabrera which assumes the migration of Cu and O ions in the formation of Cu_2O. The constant thickness of CuO, below which this variable Cu_2O layer is formed, remains to be explained. We suggest that when instability sets in, in the crystallites of CuO, because of the change in orientation, oxygen atoms or ions are able to creep in or diffuse through the interspaces between the crystallites of CuO. This diffusion results in a layer of oxygen being formed below these crystallites. Once such a layer of oxygen is produced it leads to the formation of Cu_2O according to Motts theory. The oxygen layer will be kept continuously replenished by further diffusion through the permeable membrane, now formed by the unstable crystallites of CuO. The thickness of the CuO layer or membrane below which the required oxygen layer could be formed, would be a function of the average size of the CuO crystallites, in which the instability has crept in. If the average size of these crystallites does not change appreciably, the corresponding thickness of the CuO film will not change appreciably. This also agrees with our observation viz. that the thickness of the CuO film below which a Cu_2O layer is formed is very nearly constant at all temperatures and times of formation, where such a formation is permitted.

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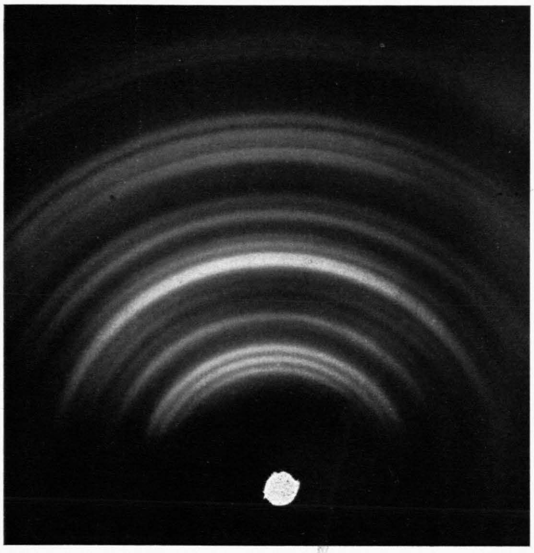

Fig. 2. Shows the three ring pattern (Δ_3).

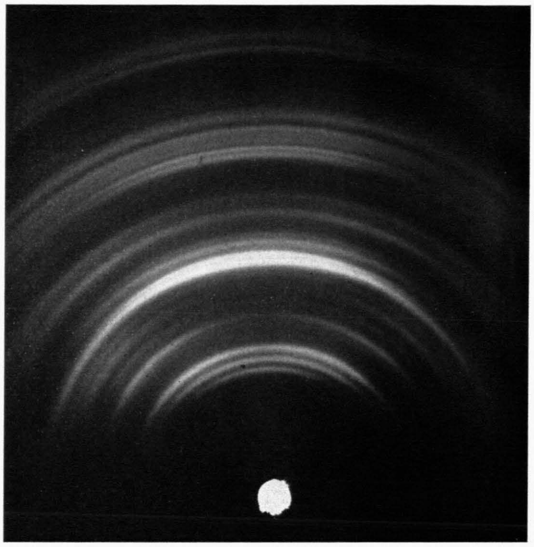

Fig. 3. Shows clear signs of the orientation of the three ring pattern (Δ_2).

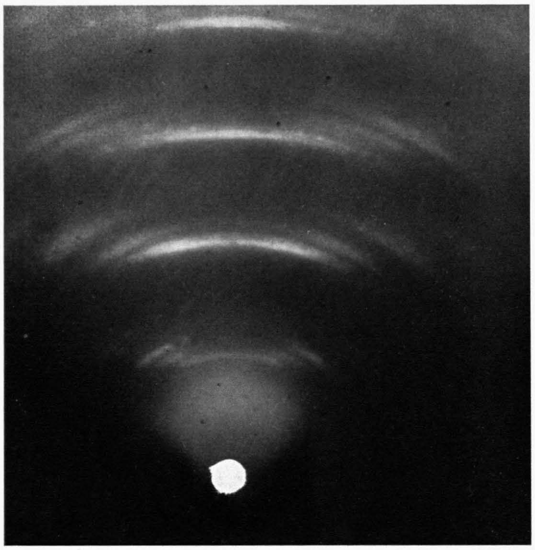

Fig. 4. Fibrous pattern due to monoclinic CuO crystallites. This also is a Δ_2 pattern with a still larger number of crystallites oriented with their diagonal planes parallel to the substrate.