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Abstract

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INFRARED ELECTROLUMINESCENCE OF CUPROUS OXIDE

1. Infrared electroluminescence of cuprous oxide was first described by Frerichs and Gandhi ([1],[2]). In their experiments a layer of cuprous oxide was located between the parent copper and a front transparent electrode. Determining the place from which the infrared radiation originated presented some difficulty. In the first publication the authors reported that the radiation arose at the p–n junction between Cu_2O and SnO_2 and was brightest when the copper plate was positive. In the detailed second publication there is no clear indication of where the radiation arises; however, the authors correlate the emission with the presence of a strong field in the barrier layer at the copper electrode and speak of an acceleration-and-impact mechanism, leading one to suppose that they abandoned the initial localization of the effect and assign its place of origin to the barrier layer, or to the layer adjacent to it, near the copper electrode.

In studying this infrared electroluminescence it was found that two types of it exist: one—the one described by Frerichs and Gandhi—arising when the voltage at the parent copper has a positive sign, and another arising in cuprous-oxide plates when the voltage at the metallic electrode has a negative sign, i.e., for the forward direction of current in cuprous oxide at the boundary with the metallic electrode. We shall denote them briefly as: the 1st type—at the parent copper —anode, the 2nd—at the metallic electrode—cathode. Some observations of the 2nd type of electroluminescence were reported in a later publication by Frerichs and Lieberman ([3]). We have obtained intense radiation effects of the 2nd type when using an aluminum cathode. It is shown that the observed bulk radiation is scattered radiation from the cathode layer.

2. **Experimental arrangement.** Strips of electrolytic copper were oxidized at 1000°C; the thickness of the cuprous-oxide layer was 0.2-0.5 mm. Either copper plates with grown cuprous oxide or cuprous-oxide plates separated from the copper were investigated. Copper oxide was removed by etching in nitric acid. A layer of tin oxide on glass served as the transparent electrode. The radiation was detected by an FEU-22 photomultiplier; the amplified photocurrent was sent to a galvanometer or an oscillograph. The electroluminescent cell and the photomultiplier were mounted in a light-tight box. An SZS-14 light filter transmitted about 6% of the cuprous-

oxide radiation. The exact composition of the radiation was determined with a UM-2 monochromator and an FEU-22 photomultiplier. The radiation maximum was located near 0.85 μ. The cuprous-oxide specimens were mounted in electroluminescent cells of the usual type (metallic electrode, cuprous-oxide plate, glass with a tin-oxide layer); for more detailed study a transverse arrangement was used (see below).

3. Using specimens with cuprous oxide on the parent copper, we obtained radiation under conditions similar to those described by Frerichs and Gandhi. A new effect was obtained when we proceeded to the investigation of cuprous-oxide plates separated from the parent copper.

An example of such measurements is given in Table 1, where i is the current and ΔB is the brightness. The cuprous-oxide specimen was clamped between two glass plates with a tin-oxide layer and subjected to a constant voltage. Four series of measurements are presented; each reported brightness value is the mean of 3–4 measurements. 1st series of measurements: the cuprous-oxide plate was clamped between tin-oxide layers; 2nd series—between the cuprous oxide and the rear electrode a sheet of aluminum foil was inserted; 3rd series—the sheet of aluminum foil was removed, conditions as in the 1st series; 4th series—pre-

Table 1

Influence of the aluminum electrode on the brightness of the infrared radiation of cuprous oxide. Measurements in an alternating-current circuit with a frequency of 50 Hz

Measurement series	Cell composition	Cell voltage, V	Cell voltage, V	Cell voltage, V	Cell voltage, V	Cell voltage, V	Cell voltage, V
		40	40	60	60	80	80
		i, mA	ΔB	i, mA	ΔB	i, mA	ΔB
1	SnO_2 | Cu_2O | SnO_2	3.5	7.5	6	41	10	144
2	SnO_2 | Al | Cu_2O | SnO_2	5	179	8.1	476	12.5	971

Fig. 1

Figure 1: Fig. 1

Measurement series	Cell composition	Cell voltage, V	Cell voltage, V	Cell voltage, V	Cell voltage, V	Cell voltage, V	Cell voltage, V
3	SnO_2 | Cu_2O | SnO_2	5.5	16	9	56	14	131
4	SnO_2 | Al powder | Cu_2O | SnO_2	3.5	223	9	1131	19	2412

···a cuprous-oxide specimen was carefully dusted on the rear side with aluminum powder; otherwise, the procedure was as in the first and third series.

A cuprous-oxide specimen between two transparent electrodes gave a small effect; for example, at a voltage of 40 V the photocurrent of the FEU-22 was $7.5 \cdot 10^{-9}$ A. Inserting a sheet of aluminum foil as the rear electrode increased the brightness by a factor of 23. Removing this sheet and restoring contact with tin oxide decreased the brightness by a factor of 11. When the oxide layer on the rear side was dusted with aluminum, the brightness again increased by a factor of 14, although the current through the cell decreased somewhat. In all these measurements the rear electrode was connected to the negative pole of the current source. Thus, the presence of an aluminum cathode substantially enhances the brightness of the electroluminescence of cuprous oxide. With aluminum as the anode, the brightness does not exceed the order of magnitude observed with tin-oxide electrodes.

Fig. 1. *a*—oscillograms of the brightness waves of Cu_2O. I—500 Hz, II—1000 Hz, III—10,000 Hz. *b*—voltage oscillograms.

Oscillograms were photographed of this radiation, obtained at an alternating-current voltage of 25 V and at frequencies up to 10,000 Hz (see Fig. 1). On the basis of the oscillograms it may be noted that: a) the electroluminescence of cuprous-oxide plates with one aluminum electrode and the other of tin oxide is practically unipolar; it occurs with the minus sign on the aluminum electrode; b) at frequencies up to 1000 Hz the phases of the radiation and the voltage

Fig. 2. Arrangement of electrodes I and II and probes I' and II' on a cuprous-oxide plate

Figure 2: Fig. 2. Arrangement of electrodes I and II and probes I' and II' on a cuprous-oxide plate

coincide; c) at frequencies up to 1000 Hz the duration of the radiation in the brightness wave is considerably less than half the period; the radiation begins after a certain voltage threshold has been reached; d) the radiation process has little inertia: at 500 Hz, 1/2000 s after the maximum, no residual radiation is noticeable; at 4000 Hz, the radiation caused by the preceding voltage phase, which had not had time to die out, was noticeable for 60 μsec after the direction of the voltage changed; the mean time constant of the relaxation process must be no more than a few tens of microseconds; e) the amplitude of the brightness wave changes only slightly with changing frequency. In Fig. 1 the amplitudes at 500 and 1000 Hz are identical, while at 10,000 Hz they are 30% smaller.

4. The electrical conditions under which the aluminum cathode was in contact with cuprous oxide were clarified somewhat by means of probe measurements. Electrodes I and II—two aluminum strips 2–3 mm wide, separated from one another by several millimeters—were pressed against the rear side of the cuprous-oxide plate; two···

point probes I' and II', each above the middle of the corresponding electrode (Fig. 2). The potential differences I—I', II—II', and I'—II' were measured. The electrodes were under a voltage of 100 V at a current of about 1 mA. In the probe circuit there was a galvanometer with an additional resistance of 118 MΩ.

At a current of 1.15 mA the potential difference I—I' with aluminum as the cathode was 10.6 V; with aluminum as the anode and the same current it was −30.6 V. Considerable brightness was observed only in the first case. In this case somewhat less than 10 V was accounted for by the potential drop across the aluminum-oxide film and the transition resistance (after subtracting the ohmic potential drop). Let us denote this potential drop near the cathode by ΔV_{k}. Figure 3 presents the dependence of ΔV_{k} on the current i. It was found that $i = C\Delta V_{\text{k}}^2$. Such an expression is characteristic of current through a thin insulating film limited by space charge. In view of the absence of the required data on the mechanism of the process at the contact of aluminum oxide with cuprous oxide, we limit ourselves to the idea that aluminum is a source of electrons injected into the cuprous oxide.

Fig. 2. Arrangement of electrodes I and II and probes I' and II' on a cuprous-oxide plate.

5. To clarify the mechanism of electroluminescence of cuprous oxide, it is essential to establish where the radiation occurs: whether it is concentrated in the near-electrode regions or arises throughout the entire thickness of

Fig. 3. Dependence of the near-cathode potential drop ΔV_{k} on the current i in a cuprous-oxide plate

Figure 3: Fig. 3. Dependence of the near-cathode potential drop ΔV_{k} on the current i in a cuprous-oxide plate

the cuprous-oxide layer (a volume effect). In the first case it is necessary to determine whether the radiation arises near the front or the rear electrode. To obtain a definite answer, we used a method that we shall call optical probing. The image of a cuprous-oxide plate, to the rear of which two aluminum strips—the electrodes—had been pressed, was projected at natural size onto a slit 1 mm wide, which transmitted the radiation to a photoelectron multiplier. The cuprous-oxide plate was mounted vertically on a stand that was moved by a micrometer screw parallel to the surface of the plate, so that successive 1-mm-wide sections from the projection of the cuprous-oxide plate entered the slit, starting from one end of it and continuing to the other.

Fig. 3. Dependence of the near-cathode potential drop ΔV_{k} on the current i in a cuprous-oxide plate.

In Fig. 4, the readings of the micrometer screw are plotted along the abscissa, and the average brightnesses of the sections along the ordinate. The total width of the plate was about 25 mm; the width of electrode I was 3.2 mm, the width of electrode II was 2.0 mm; the distance between the edges of the electrodes was 5.5 mm. A dc voltage of 300 V was applied to the electrodes. The maximum radiation was obtained when the image of the near-cathode part of the plate was projected onto the entrance slit of the photomultiplier; the radiation from the near-anode part was less than 3% of the cathode radiation. A small radiation was produced by the strip of cuprous oxide between the electrodes; it decreased in the direction from the cathode to the anode. Almost the same radiation was also observed from the opposite edge of the cathode in the direction toward the outer edge of the plate. When electrode II was the cathode, the brightness of the radiation B decreased from the cathode toward the outer edge approximately according to the exponential dependence $B = 111 \cdot 10^{-0.178(d-16)}$.

Table 2

d, mm	16	17	18	19	20	21
B_{meas}	110	77	47	33	23	14
B_{calc}	111	73.6	48.9	32.4	21.5	14.3

Table 2 compares the measured and calculated values of the brightness B. It may be assumed that this radiation is caused by scattering of rays in the bulk of the cuprous-oxide plate and their partial emergence through the front surface. Similar scattering should also occur in the interior part of the plate between the

Figure 4

Figure 4: Figure 4

electrodes. Since the brightness in this interior part did not noticeably exceed the brightness expected from scattering, there is no basis for attributing it to volume electroluminescence.

Fig. 4. Distribution of luminescence brightness along the surface of a Cu_2O plate. *I*—with electrode I as cathode, *II*—with electrode I as anode. The positions of the electrodes (on the back of the plate) are indicated by dashed straight lines.

Thus, it has been established:
a) the absence of appreciable volume electroluminescence in cuprous oxide;
b) the infrared electroluminescence effect under study arises in cuprous oxide directly at the boundary with the aluminum cathode.

In the same apparatus, various electrode materials were tested—pressed on, deposited by evaporation in vacuum, or by cathode sputtering. The strongest effect was obtained with aluminum in the form of a plate or foil pressed to the cuprous-oxide layer, or in the form of aluminum powder rubbed onto the cuprous-oxide layer, or else in the form of aluminum deposited by evaporation in vacuum. In all cases radiation was obtained when aluminum was the cathode.

6. When Al was connected as the cathode instead of tin oxide, the average value of the current changed only slightly or did not change at all (Table 1, 60 V; 3rd and 4th series), while the radiation increased 20-fold. At constant current, the number of free holes supplied per unit time to the cathode remains constant on average; at the same time, the other electrical conditions in the cuprous-oxide layer adjacent to the cathode also remain the same. The only change occurred externally, namely, the conducting layer of tin oxide was replaced by an aluminum layer covered with oxide. The enhanced electroluminescence serves as an indicator of the flux of free electrons arriving from the aluminum side, which here enter into radiative recombination. The described process of infrared electroluminescence at the aluminum cathode—cuprous-oxide boundary is very similar to the luminescence of II black carborundum described by O. V. Losev. The upper conducting layer of Losev' s "sensitive layer" is replaced here by aluminum; the lower electron-conducting layer of this sensitive layer, with high specific resistance ([4]) (the n^* layer according to Patrick ([5])), corresponds in our case to the aluminum oxide layer, and the hole-conducting black carborundum corresponds to hole-conducting cuprous oxide.

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Note: Figure translations are in progress. See original paper for figures.