Temperature Dependence of Spectral Distribution with Activation of Thermionic Emission from (Ba-Sr) O Cathodes

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Synopsis

Temperature dependence over about 750–850°K of several peaks appeared on spectral dependence over 0.6–3.5eV of thermionic emission from (Ba-Sr)O cathodes was observed with activation. Three kinds of the cathodes which were easy or difficult to activate were used as specimens. From the experiment on the three kinds of the cathodes, it was found that there were three stages in the activation process of (Ba-Sr)O cathodes, though total thermionic emission always increased with activation through the whole process. In the activation stage I, with activation, the maximum temperature of 3.2-eV peak shifted to higher temperature, though work function decreased and the intensity of each peak increased. In the stage II, with activation, work function increased on the contrary, the intensity of 3.2-eV peak decreased showing negative effect, and the maximum temperature of 3.2-eV peak shifted to lower temperature and then to higher one. In the stage III, with activation, work function decreased, the intensity of each peak increased, and the maximum temperature of each peak remarkably moved to lower temperature. From these results, it was clearly known that the earlier two stages were the abnormal stages and only the stage III was the normal activation stage.

I. Introduction

In a previous experiment[1], it was found that, besides a 3.2-eV peak several peaks which appeared over visible and infrared regions also remarkably changed in intensity with temperature over the region of 720–820°K, and that, in well activated state, a maximum existed on ΔI_{th} *vs* T curve for each peak over 3.2–1.8eV. In addition, it was expected that, a maximum of all the peaks gradually shifted towards low temperatures with activation of a cathode. In order to confirm this expectation, temperature dependence of several peaks appeared on spectral distribution of thermionic emission was observed with activation using several (Ba-Sr)O cathodes which were easy or difficult to activate.

II. Specimen and experimental method

Diodes with an indirectly heated (Ba-Sr)O coated cathode were used as test tubes. Their design was the same as those described in detail in a previous

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(1) Hibi et Ishikawa, Le Vide, **9** (1954), 121. K. Ishikawa, Bull. Res. Inst. for Sci. Meas., Tohoku Univ., **9** (1961), 211 (in Japanese).

paper[2]. The cathode coating was rectangular and had an area of about 4mm× 5mm. An anode was a rectangular nickel plate of 12 mm×14 mm with a window hole of the same area as the cathode coating for the purpose of projecting light beam onto the cathode. The anode was placed parallel to the cathode with spacing of about 1.5 mm. For activating the cathode pure heat-treatment was performed, and treatment temperature was gradually raised from about 1000°K to 1100°K with increasing activity.

An apparatus for light irradiation and a measuring circuit, which were used to observe the spectral distribution of thermionic emission, were the same as those described in detail in previous papers[2][3].

Observations were made for wavelengths at which peaks appeared on spectral distribution of thermionic emission[1]. Those wavelengths were 390 $m\mu$ (3.17eV), 530mμ (2.33eV), 620 mμ(1.99eV), 700 mμ(1.76eV), 900mμ (1.37eV), 1080 mμ (1.14eV), and 1500mμ (0.82eV),* and wavelength widths of these irradiations were 50, 70, 100, 100, 150, 150, and 150mμ, respectively.

Observations were made over the temperature 750–850°K, and this range include a cathode temperature (820°K) at which spectral distribution was observed in the previous experiment[1] on the effects of gases**. An anode voltage was 105V.

ΔI_{th} (a change in thermionic emission due to light irradiation) obtained after 30 sec of irradiation was adopted as a value of ordinate in the spectral dependence of thermionic emission***.

In order to obtain a temperature dependence of ΔI_{th} for various wavelengths, ΔI_{th} for each wavelength was first observed at a fixed cathode temperature from shorter to longer wavelength. Cathode temperature was next lowered a little and then, after an emission current became nearly stable, ΔI_{th} for each wavelength was observed again from shorter to longer wavelength. In this way, a temperature dependence of ΔI_{th} for each wavelength was obtained.

III. Experimental results

As the results of observations on several specimens, it has been found that temperature dependence of spectral distribution with activation of thermionic emission differ from specimen to specimen with respect to the degree of easiness of activation. The results will be shown in the following.

1. Specimens which were comparatively difficult to activate

By using two specimens which were comparatively difficult to activate, tem-

(2) T. Hibi and K. Ishikawa, Phys. Rev., **95** (1954), 1183. K. Ishikawa, Bull. Res. Inst. for Sci. Meas., Tohoku Univ., **9** (1961), 197 (in Japanese).

* In part of this experiment, 460mμ (2.68eV) was also observed as an aid for confirming the change of the 390–mμ peak.

** The upper limit of the observed temperature range was set due to an increase in fluctuation of emission current.

(3) K. Ishikawa, Bull. Res. Inst. for Sci. Meas., Tohoku Univ., **9** (1960), 121 (in Japanese).

*** No maximum appeared in an emission current during 30 sec of irradiation throughout this observation.

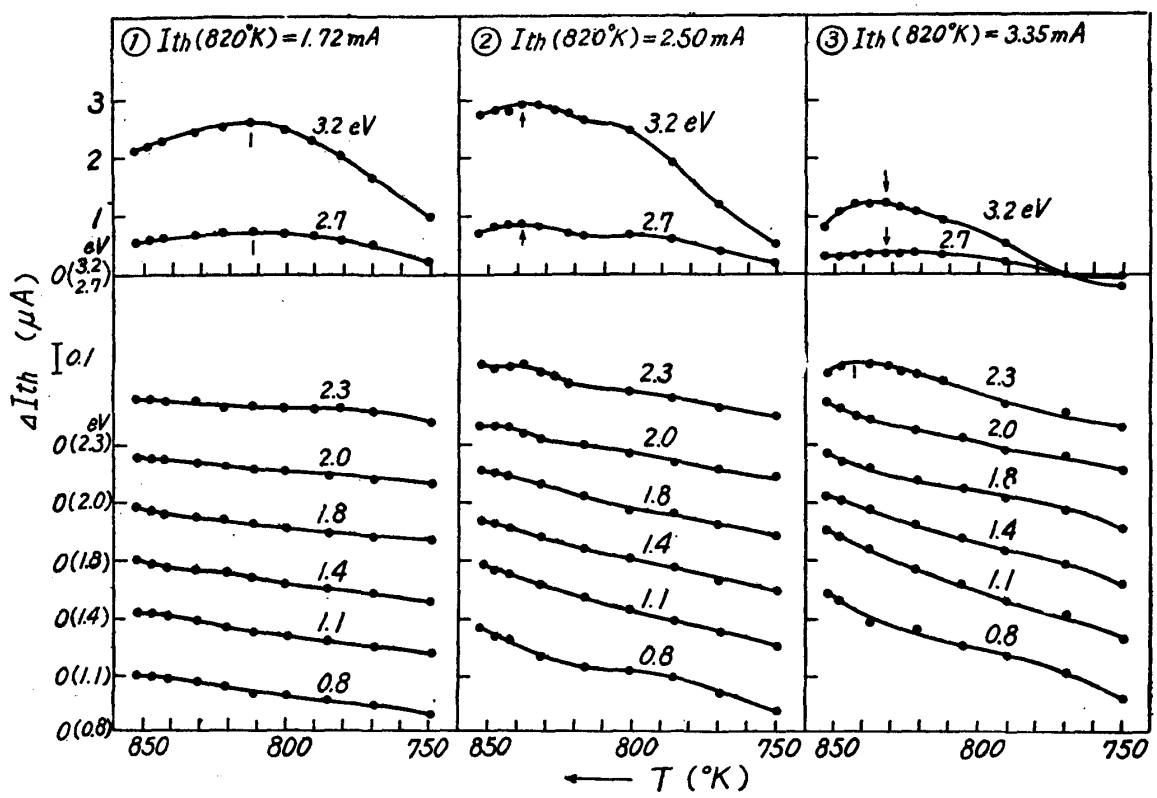
perature dependence of an intensity ΔI_{th} of several peaks appeared on a spectral distribution, total thermionic emission at 820°K, work function, and turn temperature of Richardson line were observed with increasing activation. Typical examples of the results are shown in Fig. 1 to Fig. 5. These data were obtained with the same one specimen.

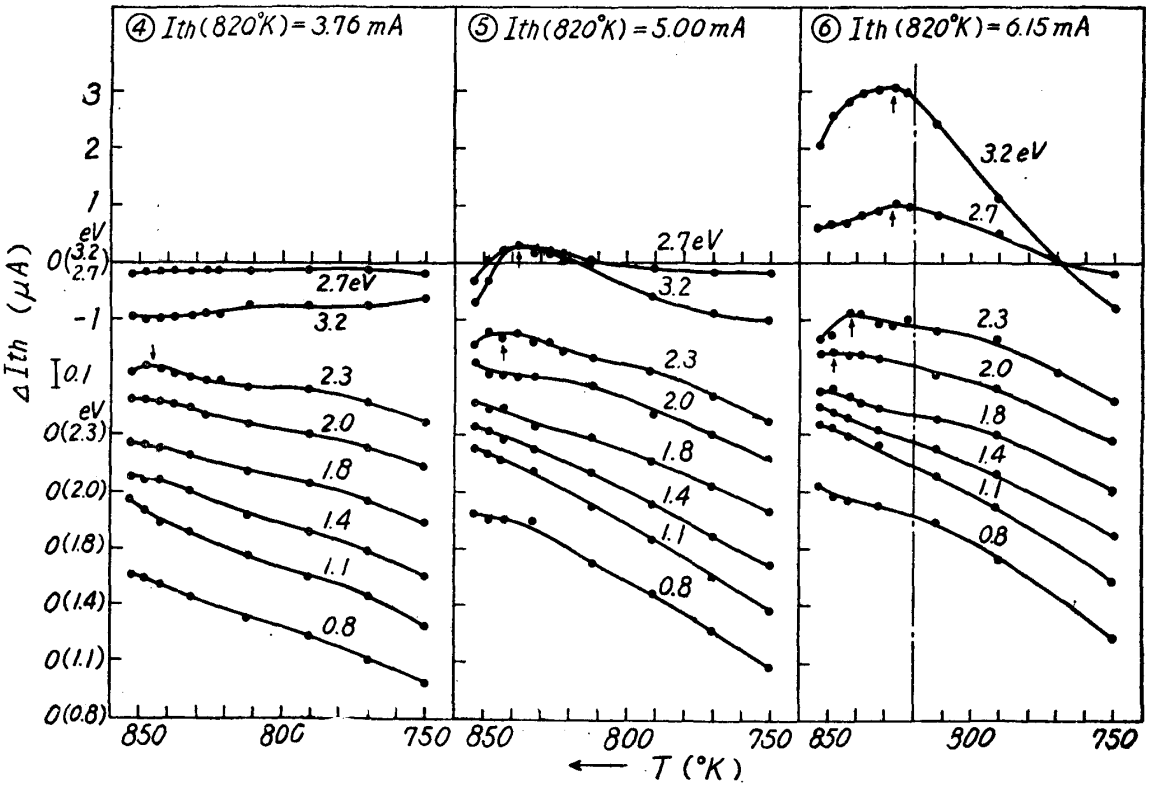
(a) Temperature dependence of spectral distribution

Fig. 1 shows a typical example of variation of temperature dependence of spectral distribution with increasing activation. In this figure, the abscissas show cathode temperature and the left-hand side is chosen as higher temperature. The ordinates show peak intensity ΔI_{th} for each peak, and the origins are shifted from curve to curve in order to avoid superposition of the curves.

The ordinates of the curves for the peak between 2.3 and 0.8eV are magnified five times as compared with those of the 3.2-and 2.7-eV peaks. Arrows and short vertical lines attached to the curves indicate a temperature at which the curves go through a maximum, and upward and downward directions of the arrows represent, respectively, increase and decrease of a maximum value as compared with that of a preceding observation. Short vertical lines indicate that a maximum value remained unchanged. ①, ②,....⑨ show an order of activation and I_{th} (820°K) represents the mean value of emission current measured at the time of beginning and end of each observation.

In the early stage of activation, as shown in curve ①, temperature dependence curves of ΔI_{th} for the peak 3.2eV and for 2.7eV showed a maximum at about 810° K, while all the other peaks over visible and infrared regions did not have a maximum and increase monotonically with increasing temperature. With activation, intensity of all the peaks increased, and the maximum of the 3.2- and 2.7-eV curves moved to higher temperatures. This movement of the maxima to higher temperature had not been expected before this experiment. The early stage of activation such as ① and ② will be called as an "activation stage I", in this paper. On further activation, the maxima for 3.2 and 2.7eV moved to lower temperature and pronouncedly decreased in intensity, showing a negative effect in lower temperature region of the curves as shown in ③. The negative effect became more pronounced, on further activation, and occurred over the entire temperature region observed, as shown in ④. At this stage, the peak for 2.3eV also lowered somewhat and its maximum moved to lower temperature, while all the other peaks over visible and infrared regions increased in intensity. The spectral dependence of thermionic emission of a specimen which was difficult to activate had been observed[2] in the earliest stage of activation, and it had been found that, with activation, the peaks of 3.2 and 2.3eV initially grew, but with further activation these peaks decreased in intensity and 3.2-eV peak showed the negative effect. The change of the 3.2- and 2.3-eV peak intensities with activation which is shown in Fig. 1, ①—④, is in good agreement with the above-mentioned facts and one can understand that such an activation stage is an abnormal one which would appear in


① Ith(820°K)=1.72mA
② Ith(820°K)=2.50mA
③ Ith(820°K)=3.35mA
3.2 eV
2.7
2.3
2.0
1.8
1.4
1.1
0.8
eV
0(3.2)
0(2.7)
0(2.3)
0(2.0)
0(1.8)
0(1.4)
0(1.1)
0(0.8)
3
2
1
0.1
ΔIth (μA)
850
800
750
T (°K)


④ Ith(820°K)=3.76 mA
⑤ Ith(820°K)=5.00mA
⑥ Ith(820°K)=6.15mA
3.2 eV
2.7
2.7eV
3.2
2.3
2.0
1.8
1.4
1.1
0.8
eV
0(3.2)
0(2.7)
0(2.3)
0(2.0)
0(1.8)
0(1.4)
0(1.1)
0(0.8)
3
2
1
-1
0.1
ΔIth (μA)
850
800
750
T (°K)

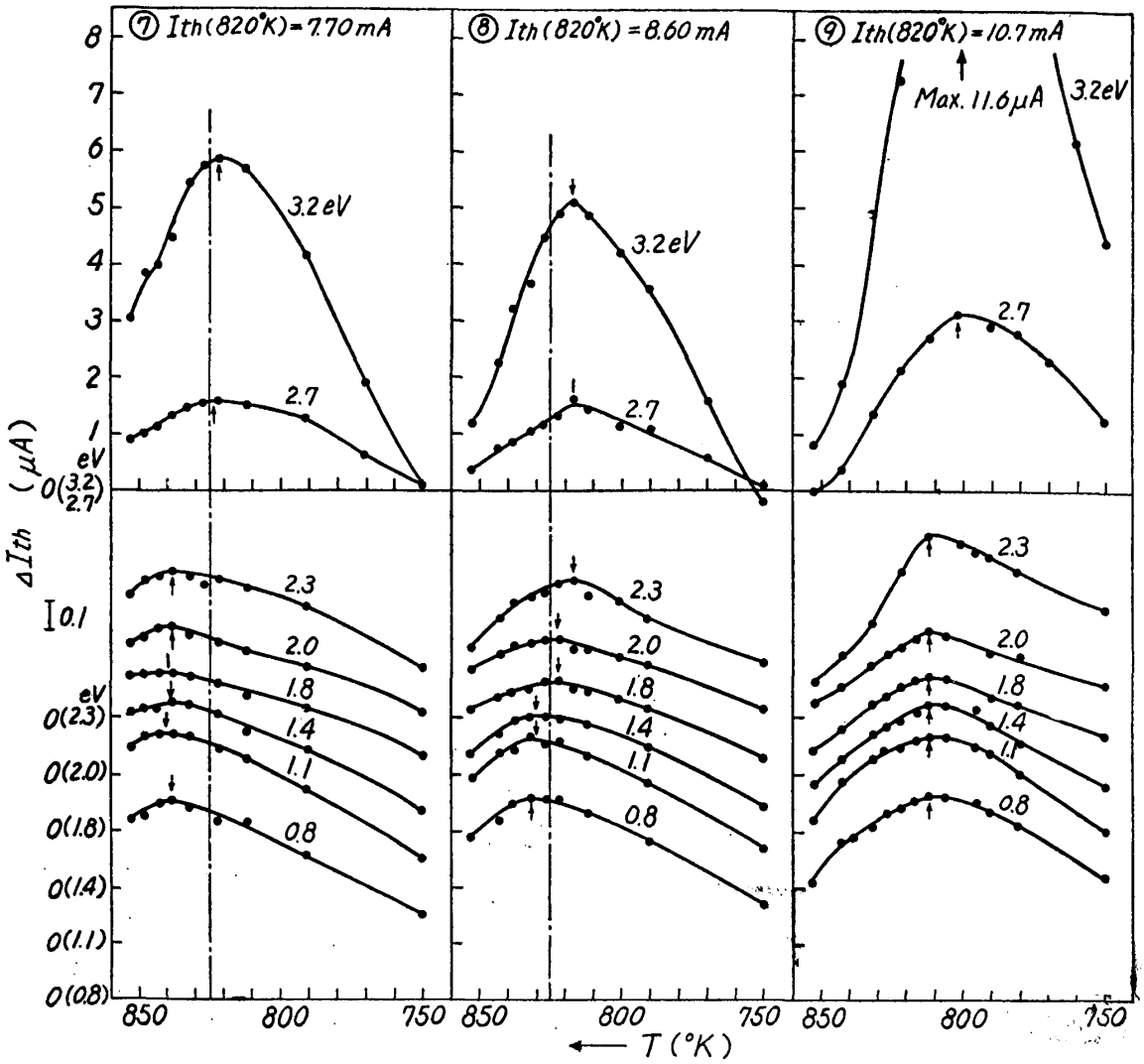


Fig. 1. The variation of ΔI_{th} *vs* temperature curve for several peaks with activation of an oxide cathode which is comparatively difficult to activate. The origin of the ordinates is shifted for each curve. The ordinates of the curves for the peak between 2.3 and 0.8 eV are magnified five times compared with those of the peak of 3.2 eV. ①, ②, ... ⑨ show the order of the observations.

the early stage of activation. The stage of ③ and ④ will be called as an "activation stage II" hereafter, since the changes in ③ and ④ much differ from those in ① and ②. From the previous results[2], it will be expected that, with further activation, a normal stage of activation will occur where all the peaks increase in intensity, and the maxima of the ΔI_{th} *vs* T curves move to lower temperatures. This expectation may be justified by the following results. With further activation, as shown in ⑤–⑨, intensities of all the peaks increased in general and maxima of ΔI_{th} *vs* T curves moved to lower temperatures. This normal stage of activation will be called as an "activation stage III" hereafter. From the above results, it has been clarified that abnormal initial stages I and II exist before a normal activation stage III.

In the states ⑤ and ⑥ which belong to stage III, maxima of all the peaks

exist at temperatures above 820°K. Assuming that a rise in cathode temperature has the same effect as an activation, therefore, the spectral distribution at 820°K should increase over the entire wavelength region. It is understood, therefore, that this state corresponds to the initial stage of activation which was observed in the previous experiment[1] with gases. In the state ⑦, maxima of 3.2- and 2.7-eV peak exist at temperatures below 825°K and those of 2.3—0.8-eV peaks appear at temperatures above 825°K, so that an inversion of the intensity of spectral distribution should occur with activation, provided that a rise in cathode temperature produces a similar effect as an activation. This change well agrees with the second stage of activation which was observed in the experiment[1] with gases. In the state ⑧, maxima of 3.2—1.8-eV peaks exist at temperatures below 825°K and those of 1.4—0.8-eV peaks exist at temperatures above 825°K, so that an inversion of the intensity of spectral distribution should occur with activation, if one assume the same as before. This change is in good agreement with the final stage of activation which was observed in the experiment[1] with gases.

In further activated stage, as shown in ⑨, the maxima of all the peaks moved to temperatures lower than 820°K. A state should exist, therefore, where the spectral distribution at 820°K decreases with activation over the entire region of wavelength. This state did not appear in the experiment[1] with gases, probably because the activation was not sufficiently progressed. It is found from Fig. 1 that maxima of the temperature dependence of ΔI_{th} appear at lower temperature in general for the peaks of shorter wavelength within an accuracy of the experiment, and that a movement of the maxima to lower temperatures is not in phase for each peak, and difference of temperature between maxima of each peak decrease in general with increasing activation.

The results which almost agree with the above-mentioned results, were obtained for another specimen which was also comparatively difficult to activate. That is, the activation stage III was reached, after passing through the stages I and II. Temperatures of the maxima differed each other, however, more pronouncedly than the above-mentioned specimen; wavelengths at which the inversion of spectral distribution occurred with activation were observed more distinctly. As a result, an inversion at 2.2eV was observed besides the inversions at 2.5eV and 1.5eV.

(b) Work function ϕ and total emission current I_{th}

Measurement was made to obtain a Richardson line immediately after an observation of the temperature dependence of spectral distribution. Fig. 2 shows the results. In the figure, ①, ②,.... and ⑧ show the order of the observations. As is seen in the figure, Richardson line has a turn and, for any state of activation, the work function ϕ_1 obtained at temperatures above the turn point is always smaller than the work function ϕ_2 obtained at temperatures below the turn point. Fig. 3(a) shows the plot of ϕ_1 and ϕ_2 against the order of the observations. In the figure, I, II, and III represent the three stages of activation mentioned above. It is found

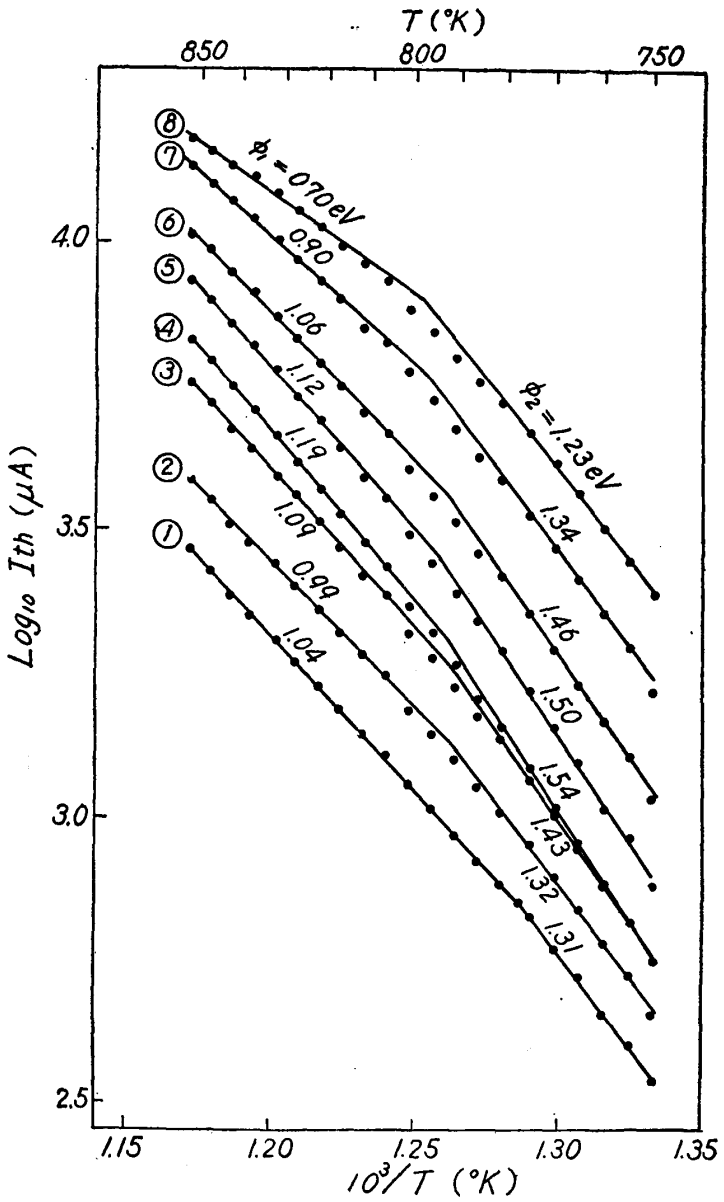


Fig. 2. The variation of Richardson line with activation of an oxide cathode which is comparatively difficult to activate. ①, ②, ... ⑧ show the order of the observations.

from (a) that ϕ_1 and ϕ_2 remain almost constant or decrease a little in the activation stage I, and they increase distinctly in the stage II, and finally decrease continuously in the stage III. Fig. 3 (b) shows a plot of average values of total thermionic emission current at 820°K at the times of beginning and end of the observations of temperature dependence of spectral distribution. It is seen from the figure that the total thermionic emission current increases monotonically with increasing activation. It can be seen, therefore, that although the total emission increases monotonically with activation, the work function changes complicatedly and abnormal initial stages I and II precede to the normal stage III in which the work function monotonically decreases with activation.

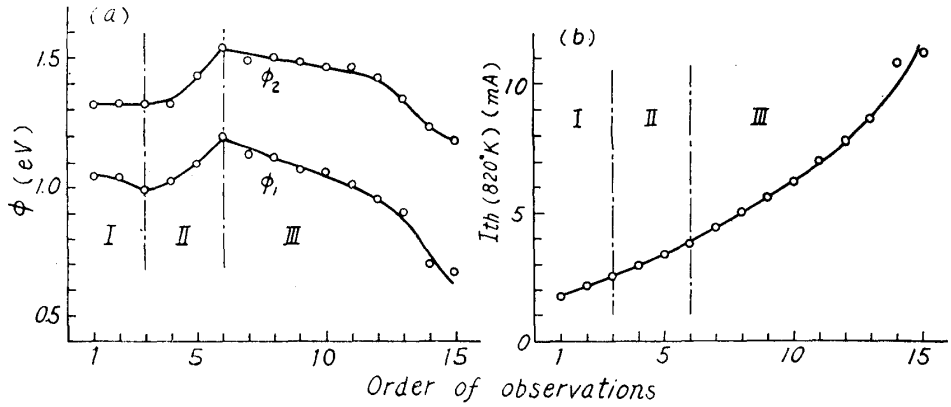


Fig. 3. The variation of work function (a) and total thermionic emission current at 820°K (b) with activation of an oxide cathode which is comparatively difficult to activate. ϕ_1 and ϕ_2 are the work functions obtained at temperatures above and below the turn point of Richardson line, respectively. I, II, and III show the three stages of activation.

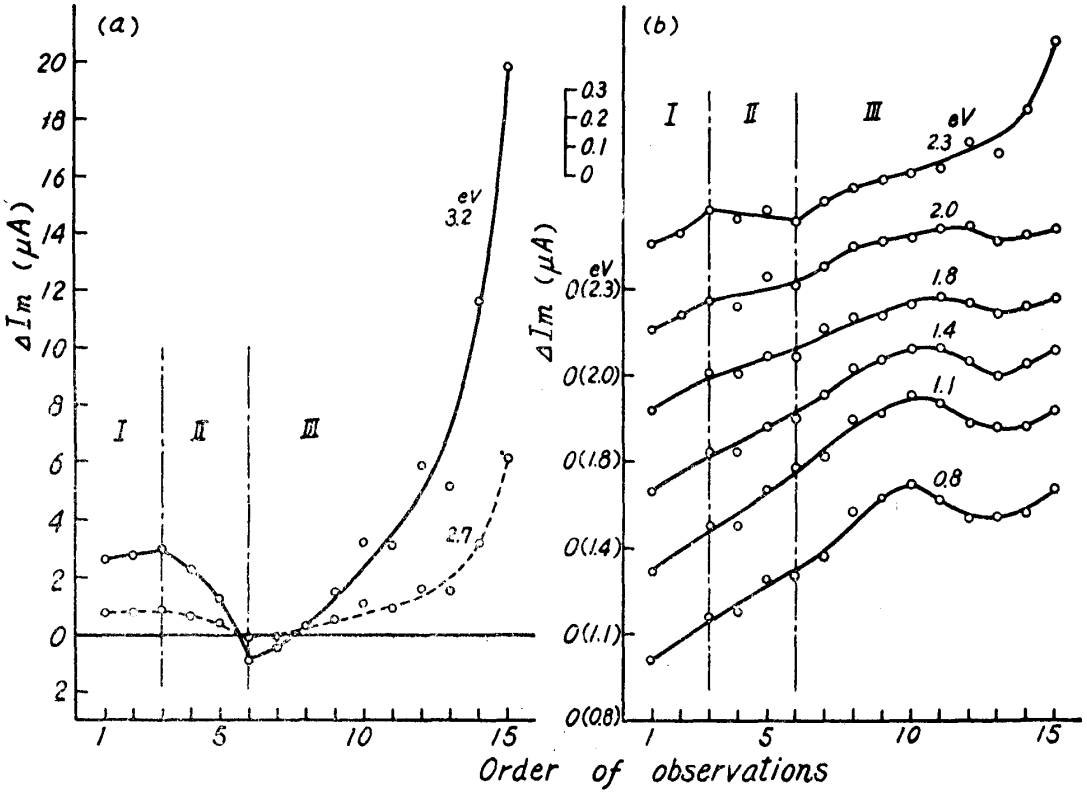


Fig. 4. The variation of maximum intensity of ΔI_{th} for several peaks with activation of an oxide cathode which is comparatively difficult to activate. In (b), the origin of the ordinates is shifted for each curve. The ordinates of the curves for the peaks between 2.3 and 0.8 eV are magnified ten times compared with those of the peak of 3.2 eV.

(c) Maximum intensity ΔI_m of temperature dependence of spectral distribution

In order to know the change with activation of the intensity of the temperature dependence of spectral dependence, the maximum intensity ΔI_m has been plotted as a function of the order of observations with activation. The result is shown in Fig. 4 (a) and (b). In the case where ΔI_{th} increased monotonically with increasing temperature within the observed temperature range, values of ΔI_{th} at the highest observed temperature (835°K) are used instead of ΔI_m. In (a), the curves are plotted using the same coordinate, but in (b) the origin of the ordinates is shifted for each curve in order to avoid superposition and the ordinate is magnified ten times as compared with (a). I, II, and III indicate the three stages of activation. As seen from the figure, in the stage I, ΔI_m of all the peaks increase with activation. But in the steag II, ΔI_m of 3.2 and 2.7eV decreases pronouncedly and show the negative effect, and ΔI_m of 2.3eV decreases slightly and ΔI_m of 2.0–0.8eV increases. In the stage III, ΔI_m of all the peaks increase in general but an abnormal phenomenon appears that ΔI_m of 2.0–0.8eV decrease and then increase in the later half of this stage. From the above-mentioned results, it is found that change of ΔI_m of 3.2-eV peak is different from those of 2.0–0.8eV peaks, and that ΔI_m of 2.3-eV peak shows an intermediate change between the above two. It is also found from the change of ΔI_m of 3.2-eV peak that the stage II is a singular stage.

(d) Maximum temperature of temperature dependence of spectral distribution T_m and turn temperature of Richardson plot T_R

In order to know the change with activation of T_m, maximum temperature of temperature dependence of spectral distribution and the relation between these maximum temperature and turn temperature of Richardson line T_R, T_R and T_m of each peak have been plotted as a function of the order of observations with activation. The results are shown in Fig. 5 (a) and (b). In the figure, I, II, and III indicate the three stages of activation. As seen from (a) and (b) in the figure, change of T_R with activation coincides pretty well with change of T_m of 3.2-eV peak, within an observed error of T_R.

As is seen from the figure, the maxima of 3.2-and 2.7-eV peak move with activation to higher temperatures in the stage I, but in the stage II they move to lower temperatures and then to higher ones, and in the stage III they move continuously to lower temperatures. In the stage I and II, therefore, the abnormal chang occurs which is different from that in the stage III. The maximum of 2.3-eV peak moves to lower temperatures in both the stages II and III, differing from the 3.2-eV peak. The maxima of 2.0–0.8eV peaks move to lower temperatures similarly to the other peaks in the later half of the stage III, though the change is not clear from the stage I to the first half of the stage III, because no maximum appeared in the observed temperature range.

2. Specimens which were very difficult to activate

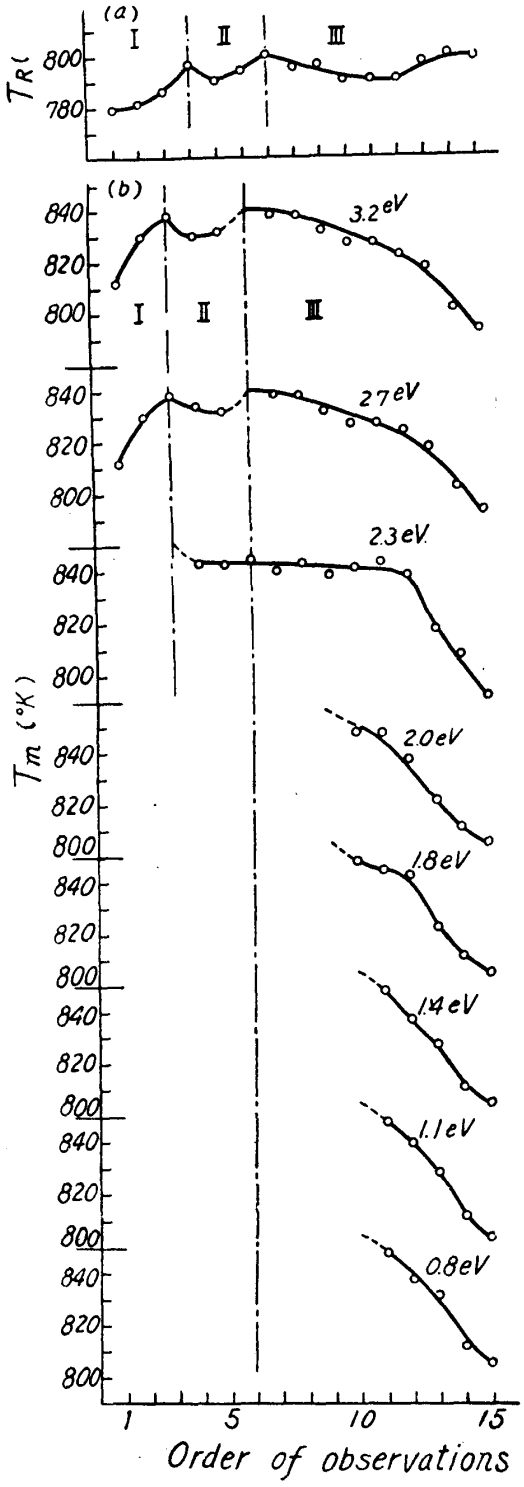


Fig. 5. The variation of turn temperature of Richardson line (a) and maximum temperature of temperature dependence of ΔI_{th} for several peaks (b) with activation of an oxide cathode which is comparatively difficult to activate.

With specimens which showed especially low emission current and were very difficult to activate among several specimens that were given the same formation treatment, temperature dependence of spectral distribution, total thermionic emission current at 820°K, and work function were observed with increasing activation. The results are shown in Fig. 6, in the same way of representation as in Fig. 1. Since, with this specimen, it was expected that the maximum of temperature

dependence will not appear up to very high temperatures, observation was carried out over 870–770°K for the data of ②–④. In the early stage of activation, 3.2-eV peak showed the negative effect and its maximum existed above 850°K, and peaks over visible and infrared regions slightly increased with rising temperature as shown in ①. After some activation, as shown in ②, 3.2-eV peak decreased and

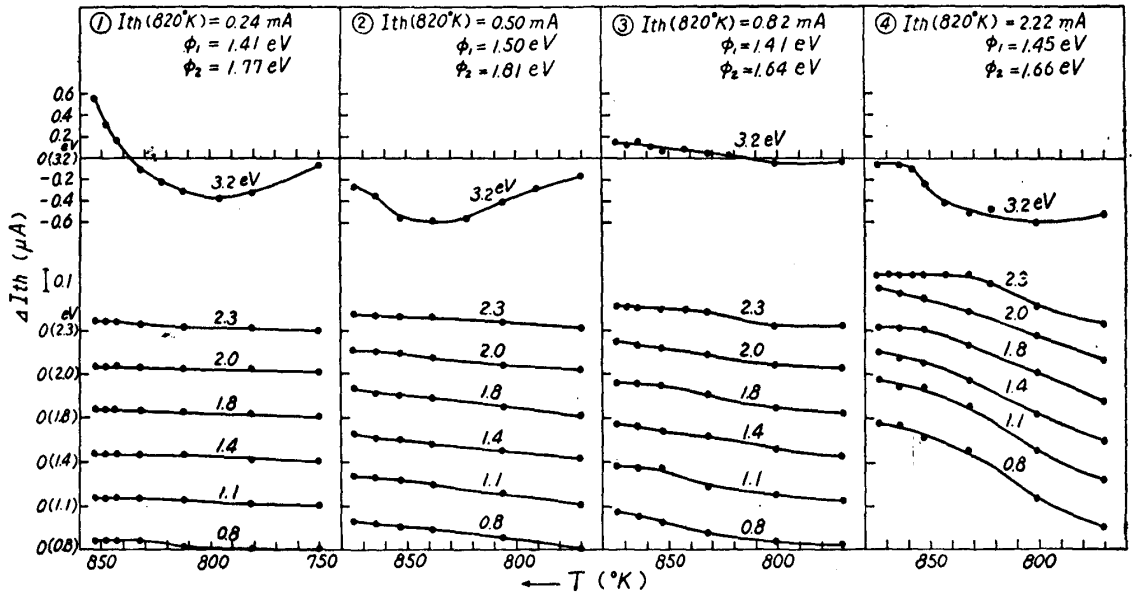


Fig. 6. The variation of ΔI_{th} *vs* temperature curve for several peaks with activation of an oxide cathode which is very difficult to activate.

showed more pronounced negative effect over the entire temperature region observed, though all the peaks over visible and infrared regions increased. In addition, the work function increased in spite of the increase in emission current. This stage clearly corresponds to the activation stage II. After further activation, as shown in ③, all the peaks increased and a decrease in work function was accompanied by an increase in total emission current. It is seen that, therefore, the activation stage III is reached at this state. On further activation, however, as shown in ④, 3.2-eV peak again decreased and showed the negative effect though all the peaks over visible and infrared regions increased, and in addition, work function increased in spite of an increase in total emission current. This shows that the state came back to the stage II. With this specimen, the activation scarcely progressed further more. In case of specimens which are very difficult to activate, therefore, it is found that the negative effect of 3.2-eV peak is very apt to appear and that the normal activation stage III is difficult to be reached and, even after the stage III is reached, the stage II soon appears again. It is noted that, in such a specimen, maxima of all the peaks appear at pretty high temperatures.

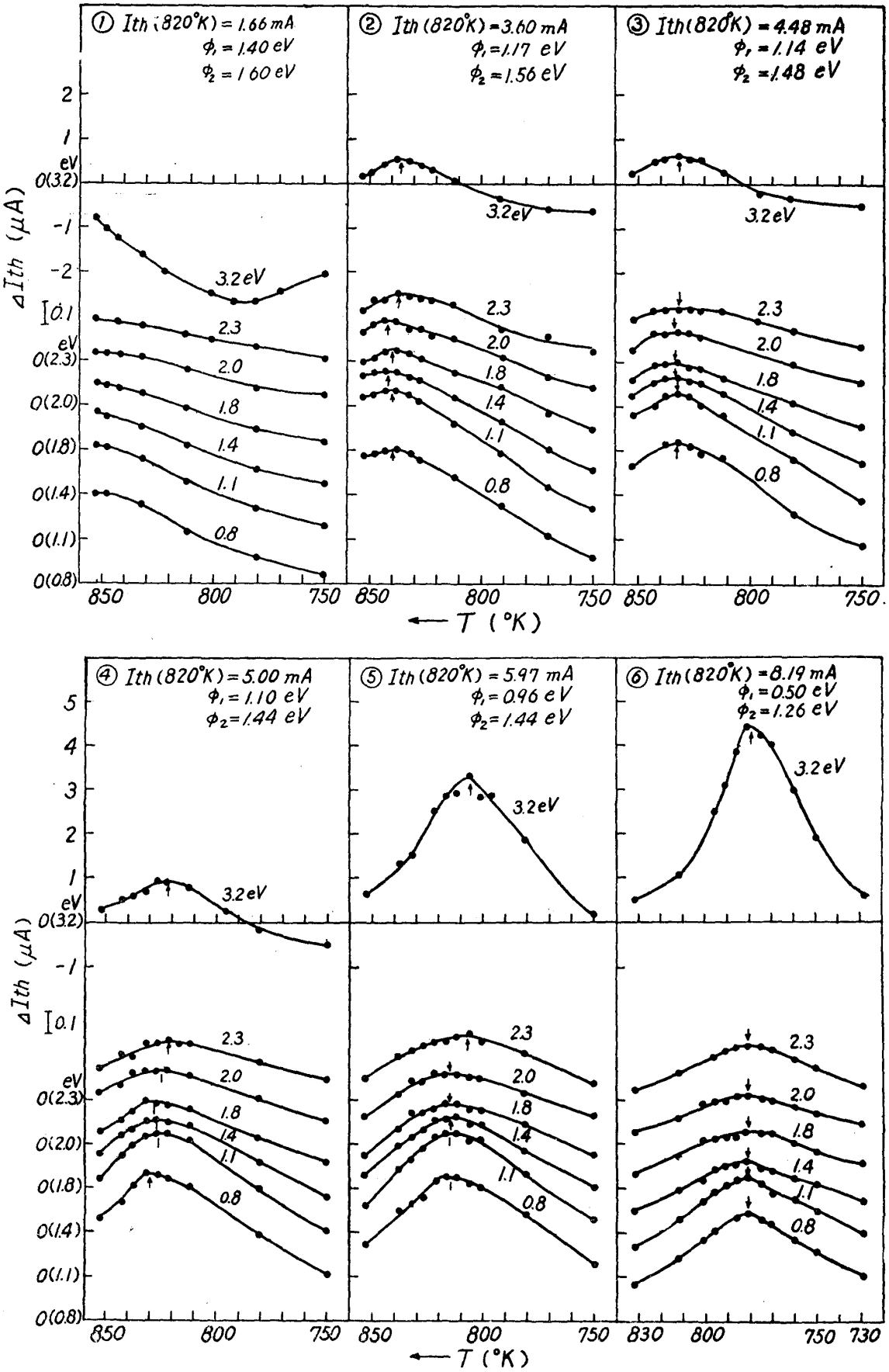


Fig. 7. The variation of ΔI_{th} *vs* temperature curve for several peaks with activation of an oxide cathode which is easy to activate.

3. Specimens which were very easy to activate

With specimens which showed comparatively high emission current and were easy to activate among several specimens that were given the same formation treatment, temperature dependence of spectral distribution, total thermionic emission current at 820°K, and work function were observed with increasing activation. The results are shown in Fig. 7 in the same way of representation as in Fig. 1. In the early stage of activation, as shown in ①, maxima of all the peaks existed at temperatures above 850°K. With activation, as shown in ②, all the peaks increased and their maxima moved to temperatures below 850°K, and an increase in total emission current is accompanied by a decrease in work function. In this specimen, therefore, the activation stage III appeared from the beginning. With further activation, as shown in ③–⑥, all the peaks increased in general and the maxima moved to lower temperatures. In addition, an increase in total emission current was accompanied by a decrease in work function and the normal activation proceeded. In such a specimen, therefore, it is seen that only the activation stage III is observed and the early stages I and II do not appear. It is noted that, in this specimen, differences in maximum temperature of each peak are small in general and that, after very well activation, maximum temperatures of all the peaks almost coincide each other as shown in ⑥ in Fig. 7.

IV. Considerations

As a result of this experiment, an activation process of oxide cathodes has been found to be divided into three stages, I, II, and III. Through the course of these three stages total emission current increases. In the stage I, with activation, a maximum of ΔI_{th} *vs* T curve for 3.2-eV peak moves to higher temperatures, while a work function decreases and an intensity of each peak increases. In the stage II, with activation, a work function increases on the contrary, and a peak intensity of 3.2eV decreases and shows the abnormal negative effect. An intensity of 2.3-eV peak decreases too, though it does not show the negative effect, and an intensity of the other peaks increases. A maximum of ΔI_{th} *vs* T curve for 3.2-eV peak moves to lower temperatures and then to higher ones. In the stage III, with activation, a work function decreases, an intensity of each peak increases, and a maximum of ΔI_{th} *vs* T curve for each peak moves to lower temperature.

The stage I is observed in the early stage of activation with specimens which are comparatively difficult to activate, and in this stage an abnormal effect appears that a maximum of ΔI_{th} *vs* T curve for 3.2-eV peak moves to higher temperatures. This effect is quite the same as those observed, in the previous experiment[2], in the early stage of activation with specimens which are difficult to activate. This is a stage that 2.3eV peak grows, which has been considered to be due to F- centers. The mechanism of activation is different, therefore, from those in the stage III in which activation proceeds due to the creation of new types of centers by an aggregation of F-centers or by a combination of it with vacainces. The fact that a maximum of ΔI_{th} *vs* T curve for 3.2-eV peak moves to higher temperatures is considered to

show an increase in stability of this center.

The stage II is a stage that appears from the beginning with specimens which are very difficult to activate. Specimens which are comparatively difficult to activate are activated also through this stage. This stage is an abnormal because the negative effect appears similarly to the experiment by McNary[4], and a work function increases with activation and also a behaviour of maximum of ΔI_{th} *vs* T curve for 3.2-eV peak is abnormal. At present, we can not physically explain this stage as well as an origin of the negative effect.

In the stage III, with activation, a work function decreases, an intensity of each peak increases, and a maximum of ΔI_{th} *vs* T curve for each peak moves to lower temperatures. This is the stage, therefore, that phenomena which were expected in the experiment with gases[1] appears clearly. It is considered that, with increasing activation, a concentration of each center increases, but a stability decreases. The phenomena observed in this stage are in good agreement with the experimental result obtained so far on the activation of oxide cathodes.

The fact that the change with activation of the turn-point temperature of Richardson line roughly agrees with that in maximum temperature of ΔI_{th} *vs* T curve for 3.2-eV peak, supports the previous experimental results[1].

Acknowledgment

The author is very indebted to Prof. T. Hibi for his helpful advice and discussion as well as the encouragement through the course of this work.

(4) B.D. McNary, University of Missouri, U.S. Office of Naval Research Technical Report No. 8 (unpublished).