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Changes In The Surface Structure Of A Single Crystal Molybdenum Point With Temperature and Applied Electric Field

by

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Notre Dame, Indiana, 14 June 1962.

Changes in the Surface Structure of a Single Crystal Molybdenum Point With Temperature and Applied Electric Field

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Bright "bars" which appear along the {111} zones of a typical molybdenum pattern at room temperature disappear and reappear again reversibly with temperature. The absence of the bars at elevated temperature is accompanied by a change in the appearance of the border of the central (110) region. This work was presented in part at the Ninth Annual Field Emission Symposium held at Notre Dame June 13-15, 1962.

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Introduction

Under the usual observational conditions of room temperature and several kilovolts applied voltage, the field emission pattern of a molybdenum crystal has a different structure from the tungsten pattern, even though both are b. c. c. with lattice parameters differing by less than 1%. On the left of Figure 1 is the tungsten pattern obtained under ordinary experimental conditions. On the right is the room temperature molybdenum pattern. Unlike the usual tungsten pattern, the molybdenum pattern exhibits brightly emitting bars, which appear along all of the [111] zone lines. (Such bars appear occasionally along the [111] zone lines of clean tungsten patterns, but they are not ordinarily as pronounced as they are in the case of molybdenum.) It is now felt that the above pattern corresponds to clean molybdenum. If the bars are possibly due to contaminant on the surface, at least they are not removed by prolonged heating of an oxygen-covered Mo tip. (1)

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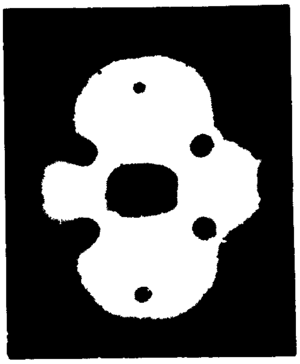
(1) D. R. Morgan, Doctoral Thesis, University of Notre Dame, Notre Dame, Indiana (1960).



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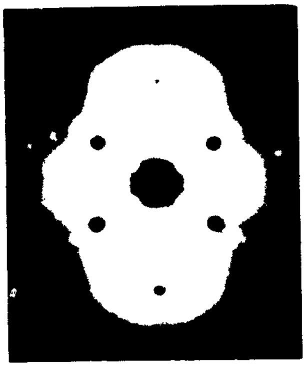

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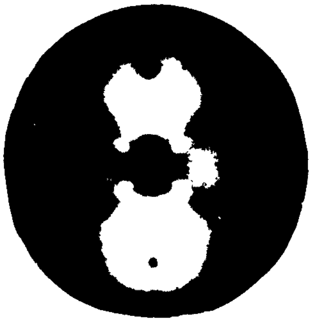
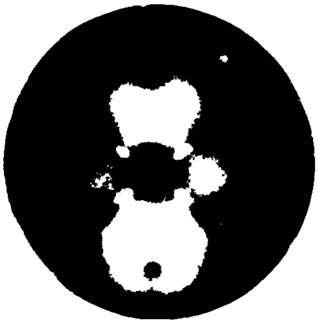


A



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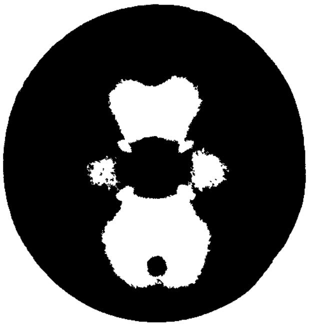

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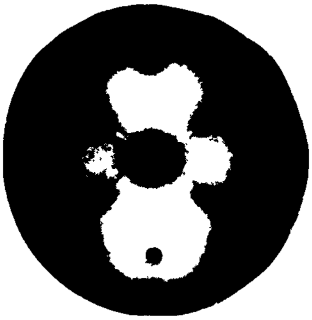

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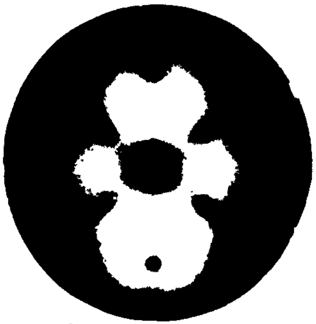


E

Figure 1

On the left is the field emission pattern from a clean single crystal of tungsten; on the right is the room temperature field emission pattern from a molybdenum single crystal.

Figure 2

Disappearance sequence for the molybdenum "bars"

Pattern	A	B	C	D	E
Time (Sec)	0	14	26	24	85
Tip Temp (^{o}K)	300	1200	1200	1200	1200

For all patterns $V_{dc} = 0$

$V_{pulse} = 14KV$

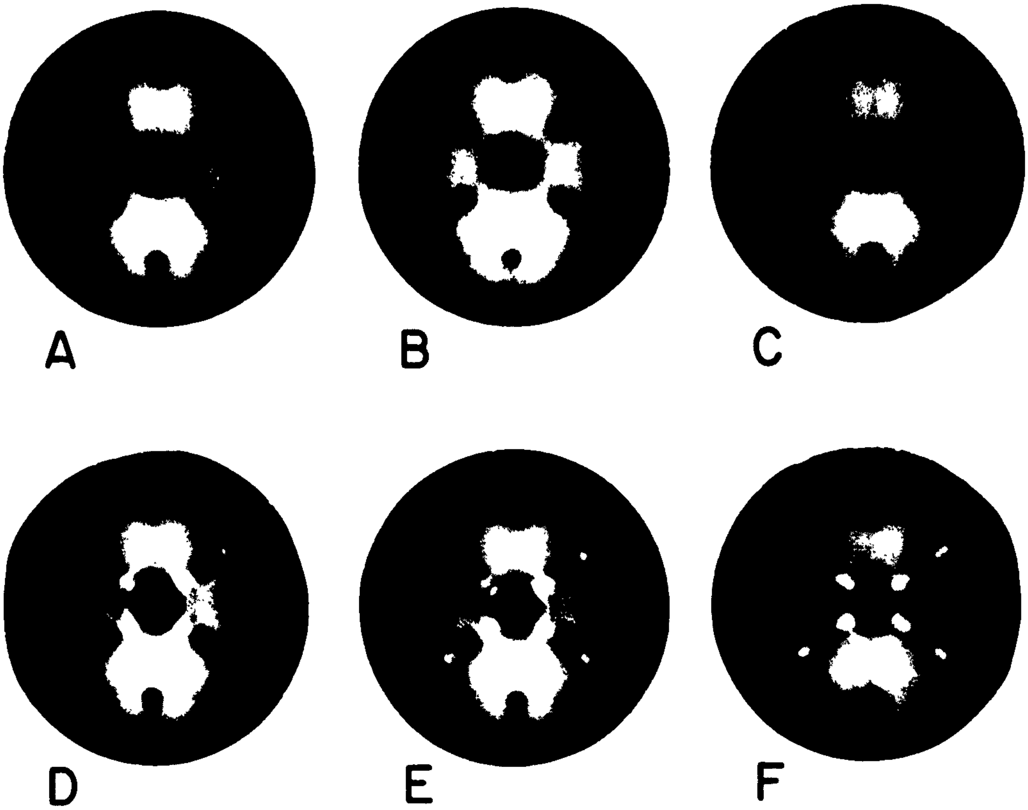
Repetition rate = 200 per sec.
Pulse width = 1.5 μ sec.

Molybdenum "Bars"

In this investigation in which the techniques of pulsed field emission microscopy were used, it was found that the bright bars present in the room temperature molybdenum pattern disappear when the field emission tip is heated beyond 1170°K.

Figure 2 illustrates a typical disappearance sequence for the bars. The conditions under which these pictures were taken are listed below. Pattern A, taken at 300°K at zero time, shows the bars very much in evidence. At this point, current sufficient to raise the tip temperature to 1200°K was turned on. Fourteen seconds later pattern B was photographed, and the bars have started to become narrower. Patterns C and D, photographed after 20 and 24 seconds of heating respectively, show that the bars have become still more narrow. By this time, there is evidence of considerable thermal agitation in the regions of barred emission. Finally, after 85 seconds of heating the last traces of the bars have disappeared, and the resultant pattern is very similar to that usually reported for clean tungsten. If the heating current is now turned off the bars reappear extremely rapidly, within one or two seconds, and pattern A again appears. So, the disappearance and reappearance of the bars is reversible in temperature.

Figure 3 illustrates the effect of a d. c. field on the heated molybdenum emitter. The d. c. voltage listed on the caption page opposite each photograph was applied, and then the emitter temperature was raised to 1240°K for the stated time. (For d. c. voltages, the emitter was negative and the screen positive. For 3KV d. c. voltage, the field at the tip is 1×10^7 v/cm., at 6KV the field is 2×10^7 v/cm., etc.) Previous to each of these runs, the tip was heated


A
B
C
D
E
F

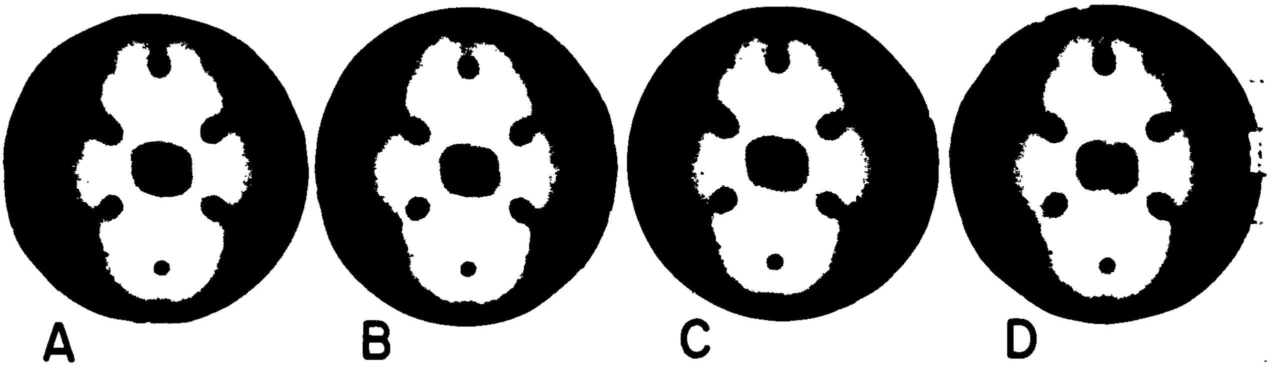

A
B
C
D

Figure 3

Effect of a d. c. field on the heated molybdenum emitter

Pattern	A	B	C	D	E	F
D. C. Voltage (KV)	0	4.5	5.5	6.1	6.6	7.0
Time (sec)	400	500	500	500	310	150

Tip Temperature = 1240°K

Figure 4

Cyclic sharp-diffuse effect for a molybdenum emitter

Pattern	A	B	C	D
Time (sec)	530	660	700	925

Tip Temperature = 1240°K $V_{dc} = 4.5$ KV to 1950°K from 3 to 5 minutes. Pattern A, taken after 400 seconds at 0 volts d.c., pattern B, taken after 500 seconds at 4.5 KV d.c., and pattern C, taken after 500 seconds at 5.5 KV d.c. indicate that voltages up to 5.5 KV have no noticeable effect on the regions of barred emission in the times given. However, as can be seen in patterns D, E, and F, voltages between 6.1 KV and 7.0 KV influence the surface sufficiently so that the bars remain. Accompanying this remaining of the bars, though, there are other field induced distortions of the patterns. Notably, the bright areas widen near the central (110), a bright ring appears about the central (110), and a step-like structure can be seen in the bars.

Cyclic Sharp-Diffuse Effect

It was during the above study that another unusual variation in the appearance of the heated emitter was noticed. This consisted in cyclic changes in the detail of the central (110) area of the molybdenum pattern, and can be described using Figure 4. After an initial heat treatment at 1950°K for 5 minutes, the emitter was set at 1240°K with a 4.4 KV d.c. voltage applied to the tip. Pattern A was photographed after 530 seconds under these conditions, and it can be seen that the border of the central (110) has a very diffuse, ill-defined appearance. By 660 seconds, the border has assumed a sharper appearance which consists in the formation of a bright ring about the central (110), the brightest parts of which lie along arcs facing the (100) planes. At 800 seconds the border is again diffuse, before becoming sharply defined once more at 925 seconds.

Figure 5 describes this "cyclic sharp-diffuse effect" numerically. With zero d.c. volts applied to the tip, the average period is 405 seconds.The effect persists upon application of a d.c. voltage to the tip, and the average period

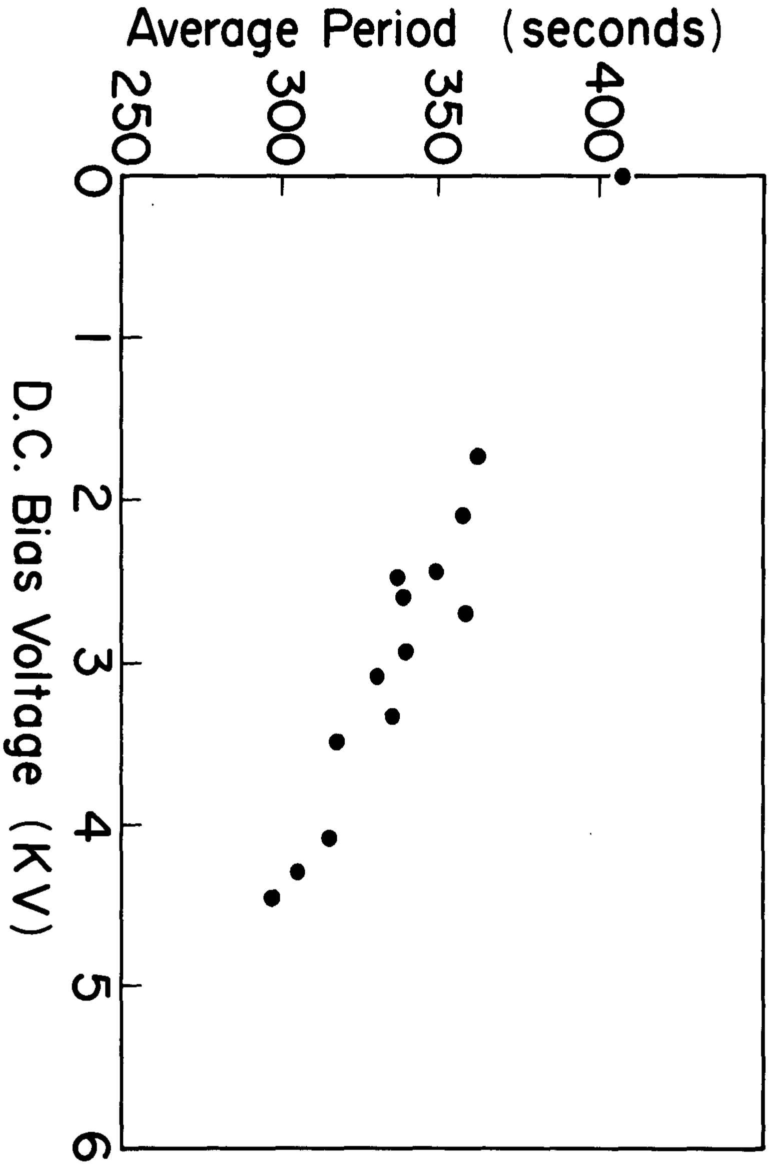

Average Period (seconds)
250
300
350
400
D.C. Bias Voltage (KV)
0
1
2
3
4
5
6

Figure 5

The average period of the cyclic sharp-diffuse effect is plotted vs. the d. c. voltage applied to the tip. Tip temperature was $1240^{\circ}K$.

decreases rather smoothly to 300 seconds at 4.5 KV ($1.5x10^7$ v/cm). A period is defined as the time between two "sharp" appearances of the (110) area.

Figure 6 is a plot of period (in seconds) vs. the number of periods for this effect when a 3.1 KV voltage is applied to the tip which is held at 1240°K. Previous to the start of the data run, the tip was flashed to 1950°K for 15 minutes and then cooled to room temperature. The first period is 245 seconds, but periods 3 to 8 represent a statistical scatter about the average period of 327 seconds. Beyond this point successive periods increase in duration, and variations in the appearance of the central (110) border become much less clearly defined. This behavior pattern is typical of our observations at different values of tip temperature and applied d.c. voltage. Almost invariably the first 1 to 3 periods are shorter than the following plateau, or average period, in the period vs. number of periods curve. It is felt that this "transient" in period duration at the start of the run (following the flash to 1950°K and cooling to room temperature) is associated with the transient observed in the tungsten disappearing rings experiment of Barbour et al. (2) The high temperature molybdenum surface structure is "frozen in" when cooled to room temperature, and then, when the tip is heated to 1240°K, temporary local rearrangements of the surface structure as it adjusts to a new equilibrium state could be expected to influence any changes in the region of the relatively small central (110). As a matter of fact, the cyclic sharp-diffuse effect itself may be just one of these temporary local rearrangements of the surface, as is evidenced by the rise in

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(2) J. P. Barbour, F. M. Charbonnier, W. W. Dolan, W. P. Dyke, E. E. Martin and J. K. Trolan, Phys. Rev. 117, 1452 (1960).

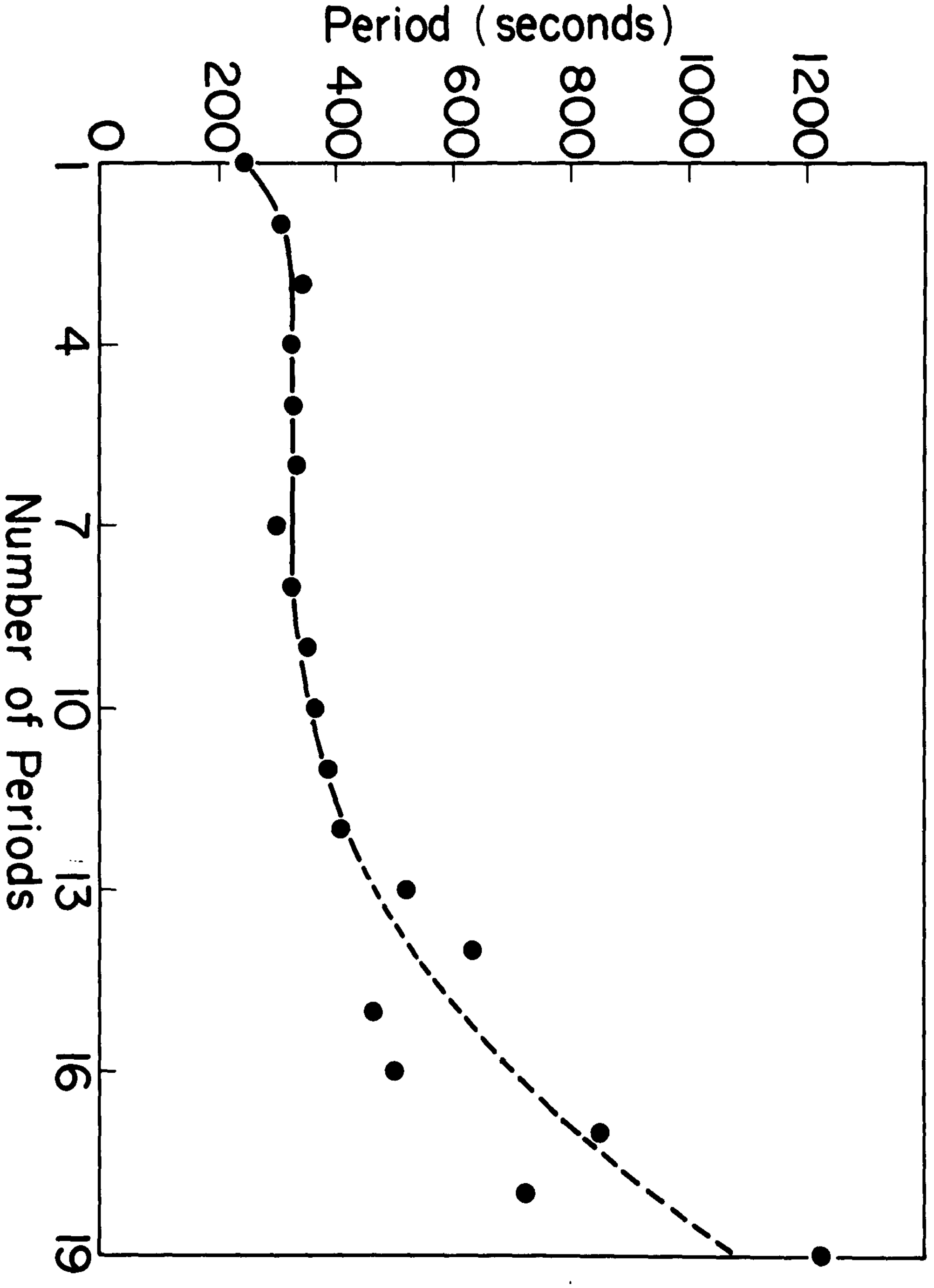
Period (seconds)
0
200
400
600
800
1000
1200
Number of Periods
1
4
7
10
13
16
19

Figure 6

The period (in seconds) for the cyclic sharp-diffuse effect is plotted vs. the number of periods observed under the condition tip temperature = 1240°K and V_{dc} = 3.1 KV.

period duration for periods beyond the average, or plateau period. This implies a gradual approach of the (110) region to a steady state condition.

With zero field applied to the tip at 1240°K, the period of this effect is nearly constant for about 4 cycles, i.e., the plateau region in the period vs. number of periods curve is 4 periods wide. Beyond this point, successive periods increase in duration. At a higher field (1×10^7 v/cm., corresponding to 3 KV d.c.) the period is nearly constant for 6 cycles before successive periods increase in duration, accompanied by much less noticeable variations in the border of the central (110). On the basis of these observations, the tendency appears to be that the number of cycles over which the period is constant increases with increasing field.

It has also been observed that a very slight enlargement of the central (110) takes place after 5 or 6 cycles with field applied, but this is difficult to measure quantitatively.

Two Arrhenius plots are given in Figure 7, in which the average period, in seconds, is plotted vs. $1/T$ ($1/°K$). For the first set of points, there was zero d.c. field applied to the emitter, and the slope of the least squares line yields an activation energy of 36.6 ± 1.6 kcal/mole. The other set of data points corresponds to the case where 3.1 KV d.c. voltage ($F = 1 \times 10^7$ v/cm.) was applied to the tip. In this case, the slope yields an activation energy of 31.5 ± 1.8 kcal/mole.

Becker (3) has observed that the (112)'s and (100)'s of a tungsten emitter held at 1200°K for 20 minutes are larger than they are after the

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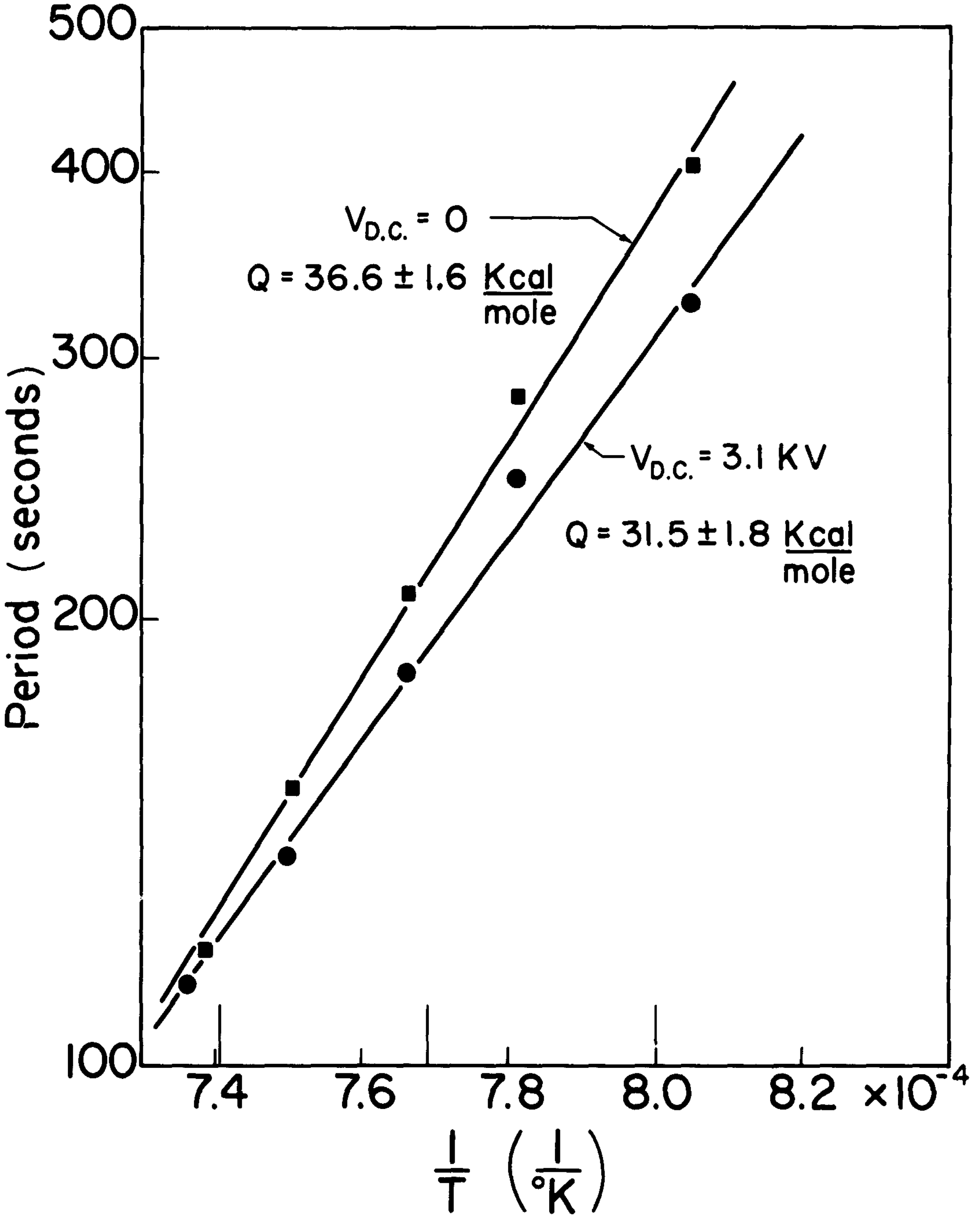
(3) J. A. Becker, Bell System Tech. J. 30, 907 (1951).



500
400
300
200
100
Period (seconds)
$V_{D.C.} = 0$
$Q = 36.6 \pm 1.6 \frac{Kcal}{mole}$
$V_{D.C.} = 3.1$ KV
$Q = 31.5 \pm 1.8 \frac{Kcal}{mole}$
7.4
7.6
7.8
8.0
8.2 $\times 10^{-4}$
$\frac{1}{T} \left(\frac{1}{°K}\right)$

Figure 7

Arrhenuis plots of the cyclic sharp-diffuse effect. The logarithm of the average period (sec.) is plotted vs. $1/T$ ($1/^{\circ}K$).

emitter has been flashed to 2400°K. In addition, the central (110) changes slightly in shape after the low temperature heating. He attributes these phenomena to a change of the tungsten emitter surface from one steady state configuration at 2400°K to another at 1200°K.

In another experiment, Strayer and Crouser (4) used the disappearing rings technique developed by the Linfield group to obtain an activation energy of 64 kcal/mole for the migration of molybdenum over a molybdenum substrate in the neighborhood of 1700°K. This activation energy corresponds to the removal of atomic layers from the (110) at the emitter apex, and a migration of these atoms over large distances and on surfaces corresponding to a variety of crystallographic directions.

The observations of Becker, coupled with our observations, lead us to associate the "cyclic sharp-diffuse effect" with the adjustment of the (110) area to its low temperature steady state configuration. So, the 36.6 kcal/mole activation energy may correspond to a local rearrangement of surface atoms rather than the large scale mass transport observed by Strayer and Crouser.

Furthermore, the decrease in activation energy upon application of a d.c. field corresponds qualitatively to the results of Bettler and Charbonnier (5) who observed the decrease in activation energy for the surface migration of tungsten over its own lattice in the presence of a high field.

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(4) L. C. Crouser and R. W. Strayer, J. Metals __13__, 74 (1961).

(5) P. C. Bettler and F. M. Charbonnier, Phys. Rev. __119__, 85 (1960).