FUNDAMENTALS OF THERMIONIC ENERGY CONVERSION
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FUNDAMENTALS OF THERMIONIC ENERGY CONVERSION[Δ]

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ABSTRACT

The achievement of the practical application of the principle of energy conversion through thermionics demands a detailed understanding of many phenomena related to electron physics. A few of these may be enumerated as (1) properties of the thermionic emitter, (2) properties of the electron collector, and (3) ionization and excitation of gas (cesium) in the interelectrode space.

Cesium vapor is most helpful as a substance in converter technology, since it adsorbs on refractory metal emitters such as tungsten or rhenium to lower the work-function and thus permits the emission of a high electron current density. Cesium is easily ionized by two methods, (1) contact with the heated emitter surface or (2) collision with high energy electrons. The ions reduce or eliminate the space-charge limitation of the available current. The collector work-function is determined by its temperature, its base material and, most of all, by the adsorbed layer of cesium.

Voltage-current curves demonstrate quantitatively the two principal modes of converter operation which are the "passive" and the "ignited," and provide the experimental data. The analysis of these data depends on the insight furnished through the application of thermodynamics and statistics to this area of research.

The final determining factors that dictate the application of the fundamental physics will be systems and materials considerations.

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GLOSSARY OF SYMBOLS

k	Boltzmann's constant 1.380×10^{-23} joule/^{o}K.
J_o	Electron current density at zero field in A/m^2. Eq. 1.
J_v	Current density in A/m^2 at any applied potential V_{app} on the Boltzmann line. Eq. 2.
q	Electron charge 1.602×10^{-19} C.
T_1	Temperature of emitter in ^{o}K. Eq. 1.
T_2	Temperature of collector in ^{o}K.
T_{Cs}	Cesium reservoir temperature ^{o}K.
V_{app}	Applied potential to establish collector Fermi level relative to that of the emitter. Generally negative. Eq. 2.
$\overline{V}$	Electron volt equivalent of temperature (kT/q).
ϕ_1	Emitter true work-function. Eq. 1.
ϕ_2	Collector true work-function. Eq. 2.

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Introduction

Energy derived from a heat source can be converted directly to electrical energy by the proper application of the principles of thermionic electron emission. To utilize this method of energy conversion, three elements are indispensable. First, electrons must be emitted from a conducting surface maintained at a high temperature. Second, the electron current must be carried by means of some transport mechanism across a gap to a collector. And third, an electron collector must be present which is maintained at a considerably lower temperature than the emitter and have a low enough work-function in comparison with that of the emitter to permit the device to deliver power to an external circuit.

The device described in these most general terms is a thermionic diode. It is not to be implied that the thermionic device which is finally shown to have the greatest utility as an energy converter will be a simple diode. At the outset, stress must be placed on ultimate objectives from an overall systems point of view. For example, one user may wish to have a converter which operates at the maximum possible efficiency, whereas another application may call for a converter which delivers the maximum amount of power per unit weight of the entire system. It is almost certain that the construction which gives the maximum power per unit weight will not be the same construction as the one that gives the maximum efficiency.

It is always the ambition of a true scientist to utilize basic knowledge in order to accomplish a specific objective. The indispensable background

of information which here is classified as "fundamental" really relates to at least three basic scientific areas. One may be identified as the fundamental physics of "microscopic" phenomena. This term is used for lack of a better one to indicate the need for detailed information concerning the physical processes involved in the actual thermionic emission of electrons from a surface. The transport phenomena depend on detailed information concerning ion generation, electron and ion space-charge and other properties associated with general concepts of plasma generation and maintenance. The work-function of the collector is again a microscopic quantity in that knowledge concerning the means by which the most suitable collector work-function can be maintained is needed. In contrast to these considerations are the "macroscopic" aspects of the problem. The designer of a converter needs to make detailed studies of the heat and electrical conduction of materials. He needs to design macroscopic configurations of these materials to minimize the heat losses and minimize the losses in power due to the ohmic resistance of the electrical conductors that serve as terminals of this energy converter. Radiation losses must be minimized and these depend on macroscopic considerations and "engineering" design. Still a third area of comparable importance has to do with the "material" problems. Long life of the device may be of extreme importance and efficiency and power per unit weight may have to be sacrificed in order to select materials that will not disintegrate or evaporate under the conditions that are dictated by the need to have extreme reliability for long periods of time.

Important though these last two areas involving fundamentals are, this discussion will be directed exclusively to the fundamentals related to the "microscopic" phenomena. Even to deal with this area comprehensively would require a book instead of an article; therefore, this treatise will simply highlight some of the problems and indicate the approach that forms the basis of extensive research programs now directed toward the achievement of energy conversion through thermionics.

An Interrelation Between Component Parts

In order to bring forward the interrelation between the components of a thermionic energy converter, Fig. 1 has been prepared. It first calls attention to the fact that the difference between the heat energy put in and the heat energy taken out is the only heat available for conversion directly to electrical power. Since this converter is thermodynamically a heat engine, the Carnot efficiency defined by $(T_1 - T_2)/T_1$ sets an absolute upper limit to the efficiency of the device. It goes without saying that this efficiency can never be attained in any practical structure. Electrical power can always be defined as the product of current and voltage. The diagram of Fig. 1 shows that the emitter and the transport mechanism predominate in the determination of the available current. The transport and the collector properties predominantly determine the voltage available. To attain the desired current density from the emitter, it must have a suitably low work-function and operate at a relatively high temperature. Unless ultra close spacing is used, electrons cannot be transported efficiently over to the collector unless positive ions are provided to neutralize the electron space-charge. Unless the collector work-function is appreciably

less than the work-function of the emitter, the output voltage when the device is operating under the condition of maximum power will be extremely low. In fact, it will be the voltage equivalent of temperature which can be computed directly as $\overline{V} = 8.616 \times 10^{-5} T_1$. At 2000°K, this voltage is 0.17 volt. To achieve a high power density, therefore, the current would have to be very large. If the difference between the emitter work-function and the collector work-function is 1.0 eV, then the available voltage could approach 1.2 volts to give six times the power for the same current.

To operate at such a high temperature at 2000°K calls for a very refractory material such as tungsten or rhenium. Either of these materials alone would yield a current density of less than 0.01 A/cm^2. Such a low current density would be hopelessly small for a practical device. The fundamental studies of Langmuir and Taylor[1] established the fact that the work-function of a refractory material can be reduced so greatly in the presence of a cesium film maintained by the equilibrium between condensation and evaporation to give an emission current density at the specified temperature higher than 10 A/cm^2.

In schematic, the diagram of Fig. 1 calls attention to the importance of having cesium present in the converter in order to establish the required low work-function for the emitter and provide for an adequately great thermionic emission current density. Clearly, if cesium will reduce the work-function of the emitter, it will also reduce that of the collector. Studies to be mentioned here show that this reduction does in fact take place by the suitable choice of materials and temperatures so that an emitter-to-collector work-function difference of at least 1 eV can be maintained as desired.

Cesium also has the property of being easily ionized. The ionization procedure depends on a combination of fundamental mechanisms. An important one is the production of ions at the emitter surface by thermal ionization. The anticipated yield of ions is well approximated by the Langmuir-Saha[2] theory. Evidence is strong that under suitably chosen operational conditions many more ions are produced by electron collisions with the cesium atoms in the interelectrode space. Generally speaking, this is not accomplished by the simple impact of an energetic electron with a neutral cesium atom. Cumulative processes are clearly evident and the fundamentals, although under present investigation, are not clearly established.

Thermionic Emission In the Presence of Cesium

Most specimens of tungsten are fabricated from polycrystalline material. Before extensive heat treatment, the crystals are very small, but the maintenance of the specimen at a high temperature results in recrystallization and the formation of much larger crystals. In order to achieve stability in the operation of thermionic converters, part of the processing should involve the maintenance of the emitter at a high temperature and for a sufficiently long period of time so that the major part of the recrystallization will have been completed.

Studies made of single crystals of tungsten reveal that the true thermionic work-function is very dependent on the exposed crystallographic direction[3]. The surface characterized by the 110 direction has a very high work-function of at least 5.3 eV and holds a cesium layer at a higher equilibrium density than any of the other surfaces. Other tungsten areas have work-functions as low as 4.3 eV. In spite of this non-uniformity in the properties of the various crystallographic faces of tungsten, the quantitative results that

describe the electron emission, current density as a function of the emitter temperature and the cesium bath temperature have been in remarkably good agreement even though the specimens used for those studies have had different heat treatment and geometrical configuration.[4]

It is important to the efficiency of a thermionic converter to have a very uniform work-function over the surface as it is operated. It is not easy to determine that the emitter work-function is uniform and a number of researches are now in progress designed to evaluate the non-uniformity associated with individual specimens operated under conditions that simulate, to some extent at least, ones likely to be found in an actual converter.

For design purposes, it is important to have available the best knowledge concerning the thermionic properties of refractory materials; therefore, the available data on tungsten used to form the chart[5] shown in Fig. 2. The independent variables are the emitter temperature and the cesium bath temperature, both expressed in degrees Kelvin. Associated with these two temperatures, an observer can determine an electron emission current density under a wide range of conditions. The Richardson type formula can be solved in terms of the emitter temperature and the observed current density to give the effective work-function. This equation is

$$\phi_1 = \overline{V} (14.0 + 2 \ln T_1 - \ln J_o) \quad . \qquad 1.$$

It is essentially by this means that the map of tungsten-cesium properties in Fig. 2 is made. The solid lines establish then a correlation between cesium temperature and emitter temperature to accomplish a specific effective work-function. The dotted lines that form "S" curves represent the emission capa-

bility expressed in A/cm^2. Across this chart, in the general region of the work-function 2.8 to 2.6 eV, are some lines that divide the chart into two important regions. The region to the left of these lines is one identified as being "electron-rich," whereas the one to the right of these lines is "ion-rich." Thus, in the absence of ions being generated in the space between the emitter and the collector, an electron space-charge sheath depresses electron emission for the electron-rich region, whereas on the right part of the diagram, an ion sheath accelerates the electrons into the inter-electrode space and suppresses the available ion production.

If the zero of the cesium temperature and the zero of the emitter temperature had not been suppressed in the layout of the coordinate scales, it would be seen that the lines tend to go through the origin of the coordinate system. It is this tendency that encourages some observers to maintain that the work-function is dependent only on the ratio (T_l/T_{Cs}). The fact that the lines do not go through the origin exactly, demonstrates that this assumed dependency on the ratio is simply a useful approximation.

Some data are available that describe the properties of molybdenum and tantalum in a similar manner[5]. The properties of rhenium are being investigated, but the details are not as yet published. Because of the dearth of well-documented information concerning the emission properties of potentially good thermionic emitters, it is still impossible to identify the emitter material most likely to be used. Not only will it be necessary to discover the most favorable emitter material, but it will be equally important to discover the best way to process this material in order to obtain the desired uniformity.

Desirable Collector Properties

Some of the desirable collector properties may be enumerated:

1. The collector work-function should be as low as possible consistent with the overall systems requirements. This point will be discussed later.

2. The collector work-function should be uniform.

3. The collector work-function should not change with time.

4. The collector work-function should not be dependent on the flow of electron current to it.

5. If the collector work-function is lowered by the presence of a complex molecular structure the film must have a negligible electrical resistance.

The collector work-function is dependent on the structure of the base material, the density of the partial monomolecular layer of cesium and on the temperature. In certain applications, specifically related to the direct conversion of heat to electricity in outer space, it will be desirable to operate the collector at a relatively high temperature in order to minimize the weight of the radiator used to discharge the excess heat. This is one of the factors that makes it exceedingly difficult to generalize concerning the most desirable work-function properties of the collector.

Analysis of Voltage Current Curves

One of the first steps that must be taken to evaluate a thermionic converter design depends on the acquisition of a voltage-current curve. For any particular test vehicle, such a curve depends on controllable parameters such as emitter temperature, cesium bath temperature, collector temperature and spacing. Uncontrolled parameters often include the detailed surface structure of the emitter and the collector, and the presence of spurious discharges that may possibly be initiated between other elements

of the test vehicle such as the surrounding walls, the emitter or collector support, and other elements that may be present in a particular device. In order to acquire information concerning fundamental mechanisms active in determining a voltage-current characteristic, it is necessary to devise a test vehicle which minimizes spurious phenomena. Such a test vehicle has been under investigation by Breitwieser[6] and has yielded valuable information. His studies have not been confined to the limited region in the voltage-current curve that corresponds to power conversion. In his studies, the collector potential may be made quite negative with reference to the Fermi level of the emitter. Under this condition at close spacing, the ion-current yield may be observed and thanks to the presence of supporting guard-rings, leakage currents may be minimized. Two typical voltage-current curves are shown in Fig. 3. One applies to the very close spacing of 10 microns and the other to the larger spacing of 460 microns. Data may be analyzed in terms of the Schottky[7] theory as it relates to ion production. Figure 4 is presented as illustrative of these results. At the close spacing of 10 microns, the observed data follow close to the theoretical line associated with that small spacing. At the larger spacings, the figure shows lines of steeper slopes than those observed at close spacing, and these indicate directly that the Schottky theory is not applicable within the range of applied voltage available before sputtering effects and other interferences set in.

The analysis of the ion-current data, combined with possible electron emission from the collector, serves as the means of separating out the electron current itself from the total observed current in the voltage-current characteristics. The plot of the logarithm of the current density as a function

of the dimensionless parameter $(V/\overline{V})$ yields additional valuable information. Four lines typical of these results are shown in Fig. 5. This means of displaying the data yields straight lines over the range in current density that corresponds to the Maxwell-Boltzmann electron energy distribution. The theoretical slope of these lines is such that for a shift in $(V/\overline{V})$ of 2.3 the electron current density changes one decade. The observed results yielded this slope quite accurately up to the Maxwell-Boltzmann limit after which the slope became less than that required by theory. This deviation from theory is a direct indication of the presence of some space-charge effect. At the very close spacing of 10 microns, the knowledge of the current density at a particular value on the Boltzmann line permits the accurate calculation of the effective work-function of the collector as given by the following formula:

$$\phi_2 = \overline{V}\,(14.0 + 2\,\ell n\, T_1 - \ell n\, J_v) + V_{app} \,. \qquad 2.$$

Figure 5 would seem to indicate that the collector work-function increases with the spacing even though its temperature and the other controllable parameters, namely, the emitter temperature and the cesium temperature, are held constant. It is our opinion that this displacement of the Boltzmann line is not a true indication of a change in the collector-work-function but simply shows that a certain fraction of the electrons, which normally in the absence of collisions with cesium atoms or ions would have crossed the interelectrode space, are turned back in the "electron-retarding" field and thus re-enter the emitter and are lost to the electron collector.

Another interesting point illustrated by the curves of Fig. 5 is that at very close spacings, the apparent saturation current is very close to 0.28 A/cm^2. This value is remarkably close to that expected on the basis of the chart of Fig. 2. Note, however, that the apparent saturation when the spacing is increased to 790 microns is 7×10^{-2} A/cm^2. The flatness of this curve indicates two things: first, a space-charge effect is limiting the current; secondly, the modulation of the space-charge by the variation of the surface potential of the collector is hardly noticeable. This means that a complex motive diagram must be assumed to exist in the interelectrode space. Quantitative evaluation of the apparent saturation establishes the location of the space-charge minimum relative to the Fermi level of the emitter.

As the applied potential is made slightly positive and the surface potential of the collector is only slightly negative with respect to the Fermi level of the emitter, ignition takes place. Inspection of the motive diagram shown here as Fig. 6 would seem to indicate that this generation of ions near the collector surface is established at a very copious rate when the electron energy available barely exceeds 2.6 eV. This is a specific example of the transfer from the "passive" mode of diode operation, in which a negligible space ionization is taking place, over to the "ignited" mode for which space ionization is dominant.

After ignition, the applied potential may be made less positive and the current observed remains practically equal to the emission capability of the emitter, as illustrated by the dotted line of Fig. 5. Very close to zero applied voltage, it is evident that the current falls very sharply. In spite of the steepness of this curve, it is retraceable as long as the minimum current

transferred across the diode does not become less than 7.5×10^{-2} A/cm^2. The ignited mode is lost when the electron current transmitted across the diode approaches within 5 percent of the current observed while it was still operating in the passive mode.

It has been the objective of this discussion to indicate that valuable information concerning thermionic diode operation can be acquired as the result of the detailed study of the voltage-current curve. To obtain this information, it is necessary to study over a very wide range of applied potentials, so that the various components of current can be separated. It is not easy to make this separation in a completely unambiguous manner. Small details should not be overlooked since they may have a very important bearing on the determination of the real mechanisms controlling the converter performance.

Conclusions

It has been the purpose of this presentation to stress the need for further research to establish the fundamental "microscopic" properties of the materials useful in thermionic energy converters. The factual data presented serve mainly as an indication of the researches now in progress and the research results anticipated in the near future. Important decisions basic to the successful development of practical energy converters cannot be made on anything but a cut-and-try basis without the necessary back-up of fundamental information. Even when this is available, there will still be important problems to be solved that relate both to the properties of the materials useful in this area and to the design and construction of units best adapted to fit into an overall converter system. The thermionic converter itself is only a component even though an important one and in the long run cannot be divorced

from the other components which include the source of heat and the means of discharging the unused thermal energy into some form of heat sink. In terrestrial applications, this heat sink might very well be another energy converter and in that sense, the thermionic converter would be a "topping unit." In space applications, the heat sink will probably have to be a radiator and in order to minimize its weight, it will be necessary to operate this radiator at the highest possible temperature consistent with a reasonable overall efficiency of the system as a whole.

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FIGURE CAPTIONS

Fig. 1. Block diagram to show interrelation between elements of a thermionic converter.

Fig. 2. Emission properties of tungsten. Solid lines: work-function related to emitter temperature and cesium temperature. Dotted lines: current density in A/cm^2. Double dot-dash line: demarcation between electron-rich sheath on the left and ion-rich sheath on the right as given by Langmuir-Saha equation. Plus-dash line: demarcation between stable and unstable region. To the right of line ions must be returned to the emitter to obtain stable results.

Fig. 3. Two voltage-current curves taken by Breitwieser. Emitter temperature 1500°K, cesium condensation 500°K. Solid line spacing: 460 microns. Dash line spacing: 10 microns. Note change in voltage scale for ion currents shown negative. Current density anticipated from chart of Fig. 2 is i_o. MBL limit of Maxwell-Boltzmann distribution. Passive mode range d to e: quasi saturation due to limiting barrier. Ignition at f. Range g to h: ignited mode before arc mode at i. Ignited mode returned toward passive mode j to k. Line may be retraced if k remains 5 percent above passive mode line.

Fig. 4. Ion currents plotted on the basis of the Schottky mirror-image theory for ion current increase with applied voltage. Six spacings shown from 10 microns to 790 microns. (L-S · 2): anticipated ion current based on Langmuir-Saha theory. ISO: random current in isothermal diode. (1): Langmuir-Saha equation with statistical weight of 2 omitted.

Fig. 5. Electron currents plotted according to Maxwell-Boltzmann energy distribution analysis. Emitter 1500°K, cesium 500°K. Limit of Maxwell-Boltzmann range shown by +. Dashed lines: space-charge theory applied to an ion-free electron emitter. Dotted line: return from ignited mode toward passive mode for the spacing 790 microns. ISO: random current density expected in an isothermal diode.

Fig. 6. Hypothetical motive diagrams applicable to spacing of 450 microns, temperatures 1500°K and 500°K. Surface potential of the emitter relative to its Fermi level shown by left-hand dot. Collector surface potentials shown for six different values of applied potential. Collector work-function 1.8 eV. Note intermediate space-charge barriers not easily modulated. Important changes in the collector sheath are shown.

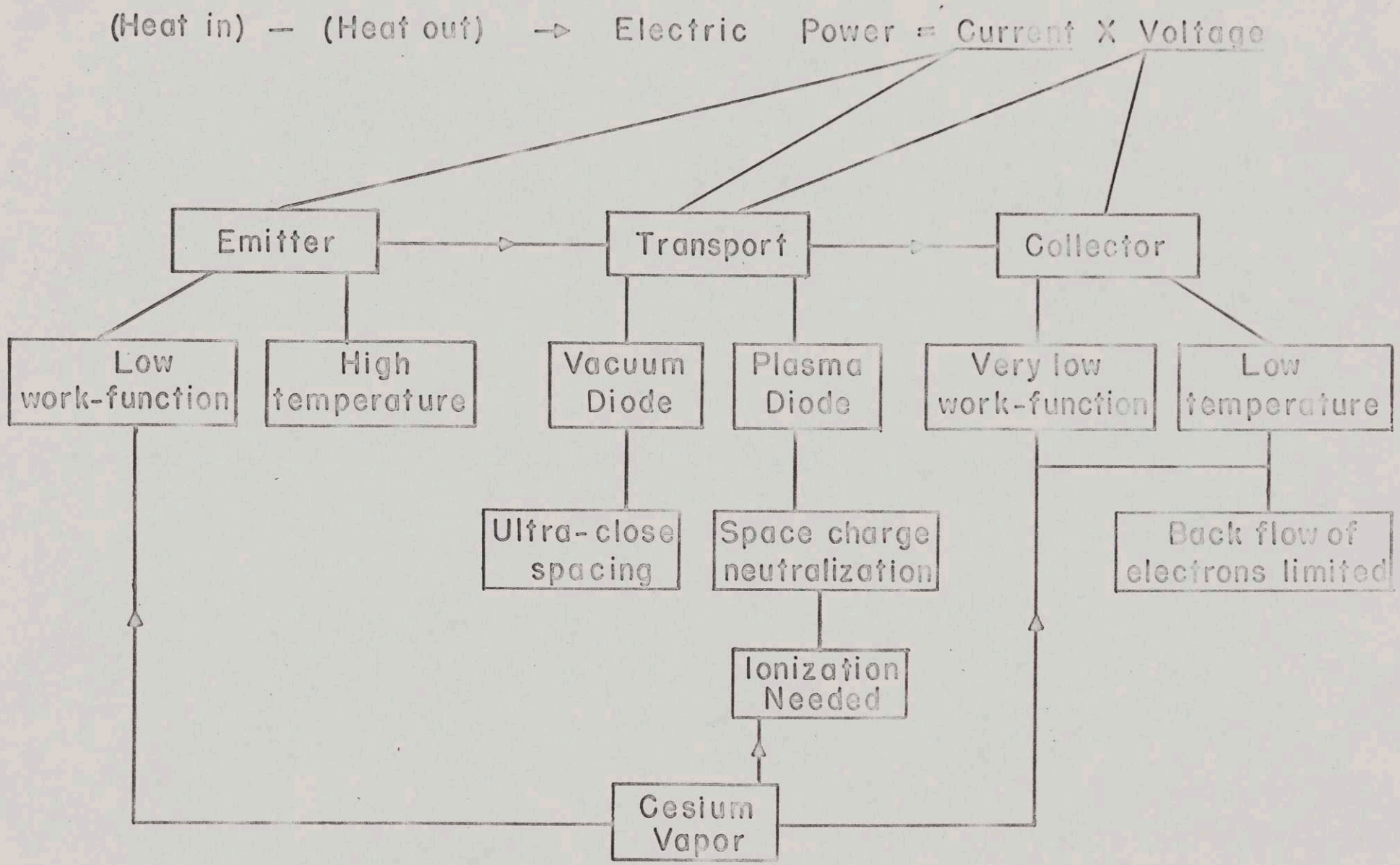
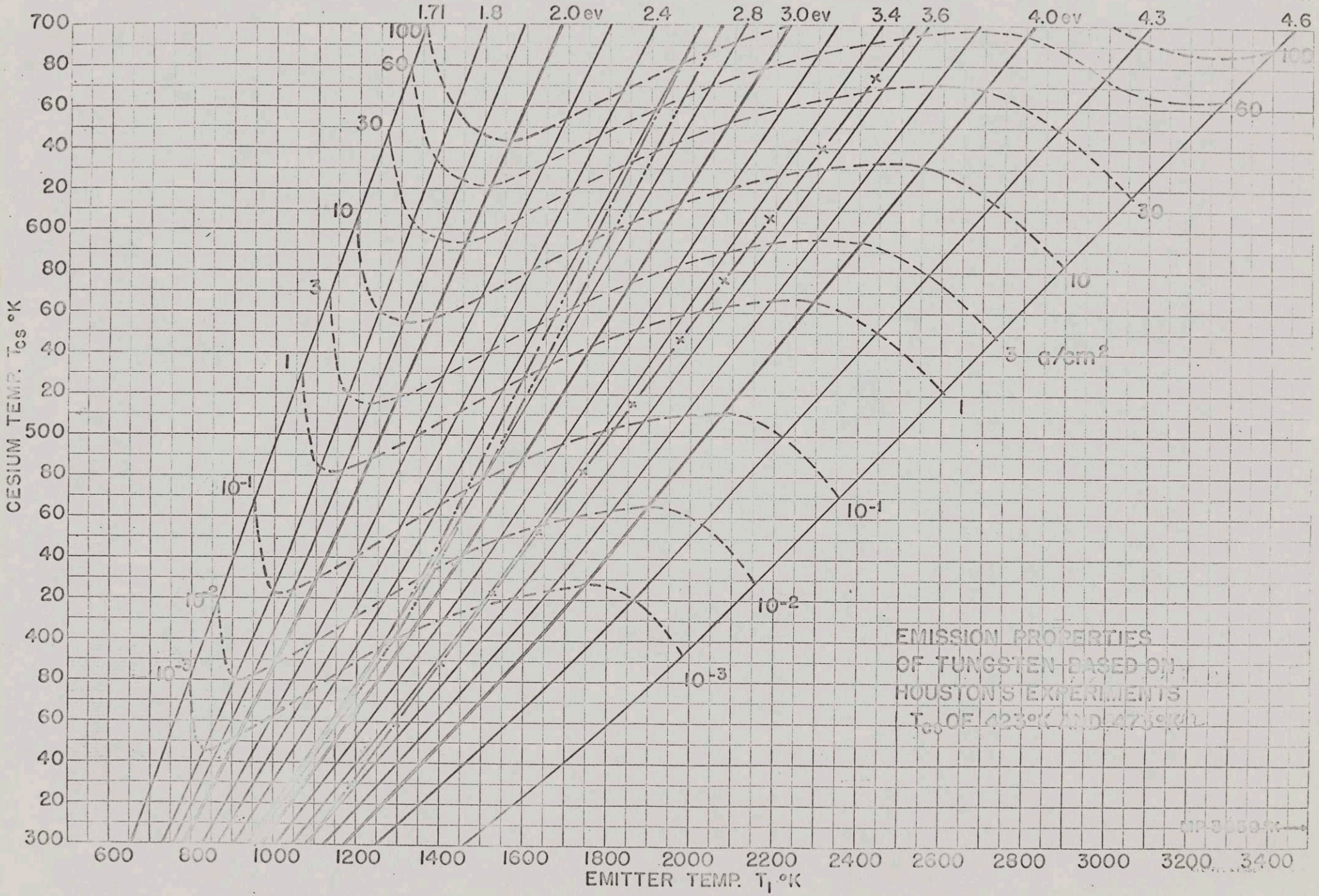

(Heat in) — (Heat out) → Electric Power = Current X Voltage
Emitter
Transport
Collector
Low work-function
High temperature
Vacuum Diode
Plasma Diode
Very low work-function
Low temperature
Ultra-close spacing
Space charge neutralization
Back flow of electrons limited
Ionization Needed
Cesium Vapor

Fig. 1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1.8
2.0 ev
2.4
2.8
3.0 ev
3.4
3.6
4.0 ev
4.3
4.6
100
60
30
10
3
1
10-1
10-2
10-3
3 a/cm²
CESIUM TEMP. Tcs °K
EMITTER TEMP. T1 °K
EMISSION PROPERTIES
OF TUNGSTEN BASED ON
HOUSTON'S EXPERIMENTS
Tcs OF 423°K AND 473°K

Fig. 2

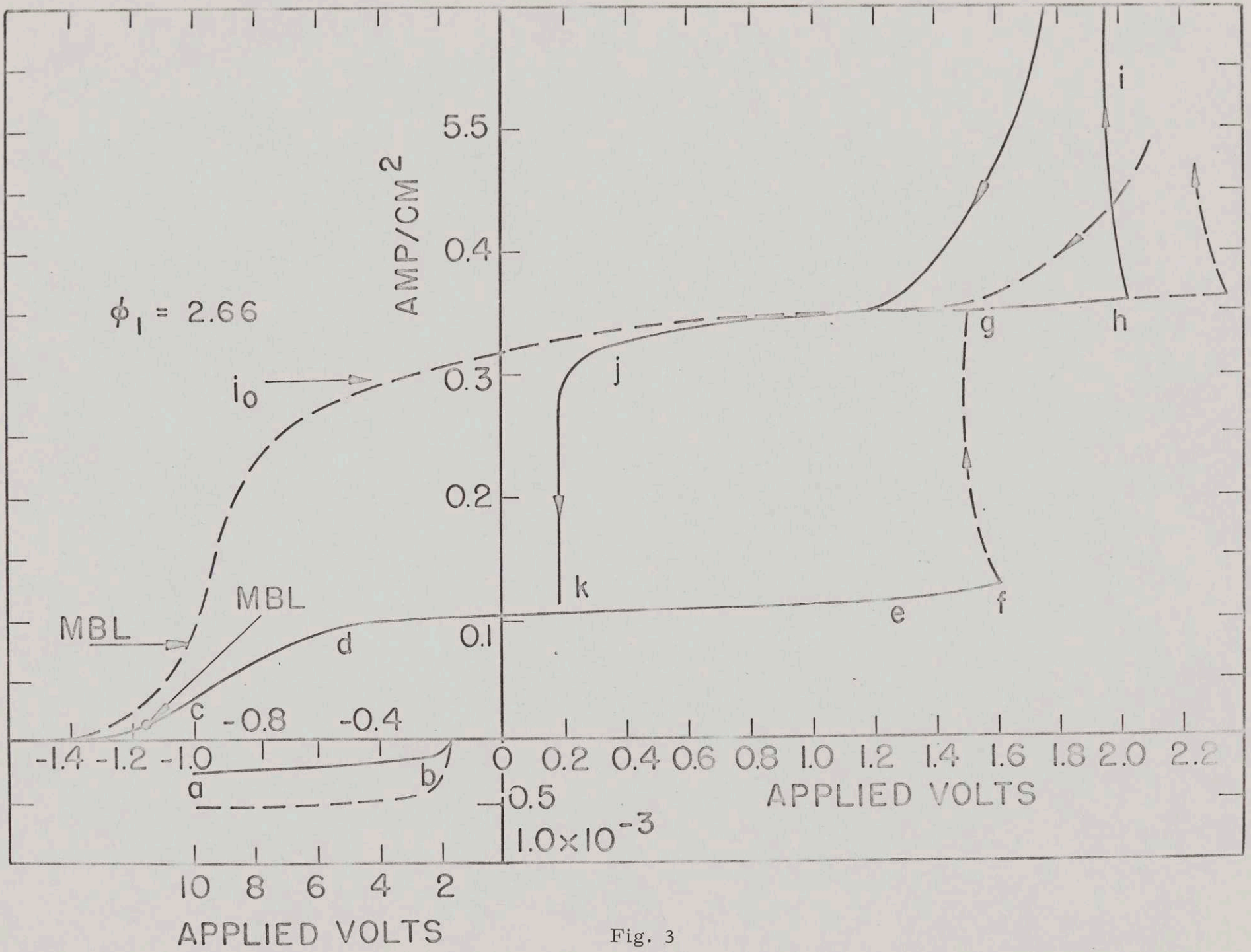
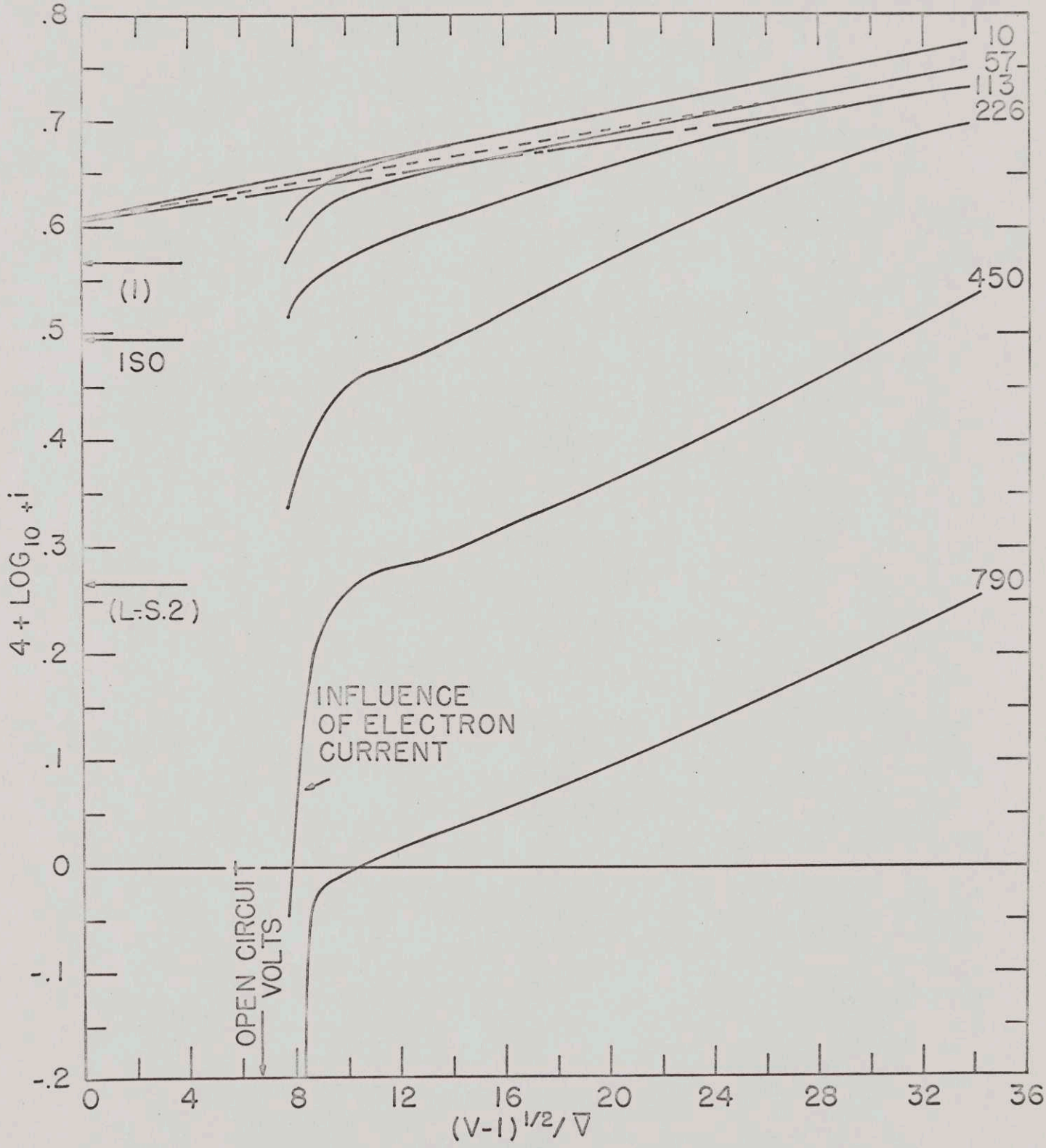

ϕ_1 = 2.66
AMP/CM^2
5.5
0.4
0.3
0.2
0.1
i_o
MBL
MBL
d
c
-0.8
-0.4
-1.4 -1.2 -1.0
a
b
10 8 6 4 2
APPLIED VOLTS
i
j
k
g
h
e
f
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2
APPLIED VOLTS
0.5
1.0×10^{-3}

Fig. 3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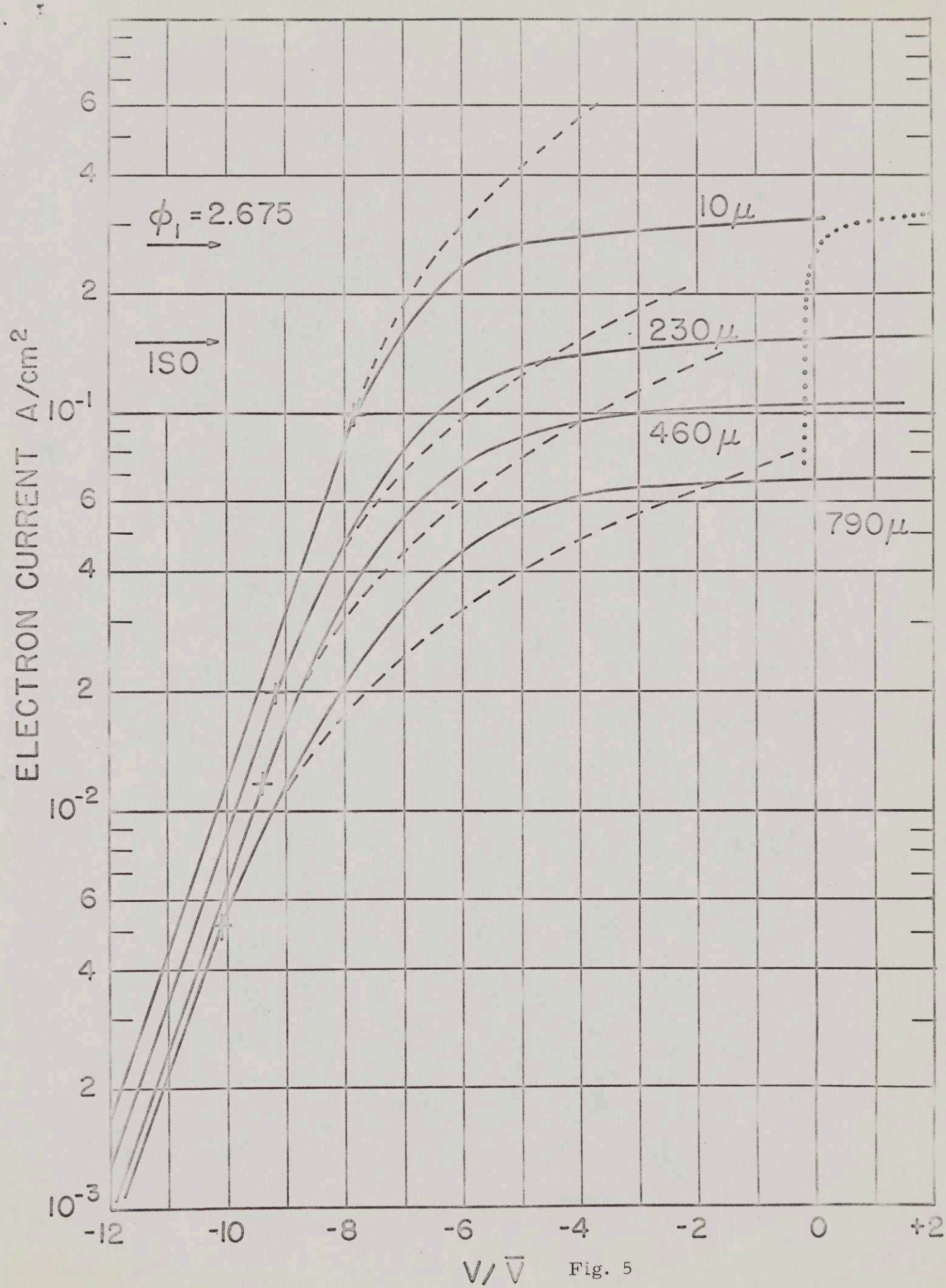
4 + LOG10 i
10
57
113
226
450
790
(I)
ISO
(L-S.2)
INFLUENCE
OF ELECTRON
CURRENT
OPEN CIRCUIT
VOLTS
0
4
8
12
16
20
24
28
32
36
(V-I)1/2/ ∇

Fig. 4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ISO
10μ
230μ
460μ
790μ
6
4
2
10^{-1}
6
4
2
10^{-2}
6
4
2
10^{-3}
-12
-10
-8
-6
-4
-2
0
+2
V/$\bar{V}$

Fig. 5