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Enhancement of thermionic emission by light

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Abstract. In this paper the rate of electron emission from an illuminated hot metallic plate has been evaluated on the basis of the free electron theory of metals and Fowler's theory of photoelectric electron emission. The modification of the electron energy distribution (or enhancement of electron temperature) in the plate by energetic electrons (which get their normal energy enhanced on the surface by incident photons of frequency below threshold and are not emitted) has been taken into account. The thermionic current as modified by the electron temperature so enhanced by irradiation has been evaluated. The results may be applicable to thermionic convertors, as proposed to be operated by Schwede et al. [J.W. Schwede, I. Bargatin, D.C. Riley, B.E. Hardin, S.J. Rosenthal, Y. Sun, F. Schmitt, P. Pianette, R.T. Howe, Z. Shen, N.A. Melosh, Nat. Mater. **9**, 762 (2010)]. Numerical results have been presented and discussed.

1 Introduction

There has been considerable development [1,2] of thermionic energy converters (TEC) since the fifties of the previous century. The motivation was in the context of the requirement of high power autonomous generators for deep space missions and possibly some terrestrial applications. Compatibility with high cathode temperatures and large current densities, required for efficient operation of the device for intended applications has been an ever present challenge [3,4].

A simple thermionic convertor consists of a hot cathode and a cooler anode, separated by a vacuum gap. An interesting concept for the enhancement of the current density from the cathode has been advanced by [5,6] viz illumination of the cathode ("p" type semiconductor) to enhance the electron density by photo excitation of electrons in the valence band and thus causing the Fermi level to go up and effectively lower the work function. The theory is basically a qualitative one and is just confined to the evaluation of thermionic current by an arbitrary increase of Fermi energy; the photoelectric current is ignored. However, semiconductors are not suitable for high temperature applications.

To explore the phenomenon quantitatively in metals, which can operate at high temperatures we follow the free electron theory [7] of solids (particularly appropriate for metals) and Fowler's theory [8,9] of photoelectric emission of electrons, which is the earliest and most frequently used one. According to Fowler's theory [8,9] an electron, incident on the surface ($x = 0$) from inside the plate has a probability β per photon incident per unit area in unit time, of getting its normal energy $E_x = p_x^2/2m_e$ enhanced by $h\nu$, where p_x is the normal to the surface component of the incident electron momentum, m_e is the mass of an electron, h is Planck's constant and ν is the frequency of incident light. We may consider two possible scenarios as follows:

1. Out of electrons incident on the surface from inside, a fraction $[1 - \beta(\nu)\Lambda(\nu)]$ does not interact with photons and gets emitted when the normal energy $E_x > W_a$, the height of the surface energy barrier; such an emission may be called the classic thermionic emission. The parameter $\Lambda(\nu)$ is the number of photons, incident on the surface per unit area per unit time and $\beta(\nu)$ a parameter, characteristic of the metal; with cm^2 s as unit. As $\Lambda(\nu) \to \infty$ the probability term $[1-\beta(\nu)\Lambda(\nu)]$ should be replaced by $[1 - \beta(\nu)]^{\Lambda(\nu)}$.
2. A fraction $\beta(\nu)\Lambda(\nu)$ of electrons incident on the surface have the normal energy enhanced by $h\nu$. Out of these electrons, those with an energy E_x, given by $(E_x + h\nu) > W_a$ get emitted (photoelectric emission) while the rest with $(E_x + h\nu) < W_a$ remain a part of the free electron system in the metal, causing a higher electron temperature and consequently enhanced thermionic emission. When the frequency of incident light is below threshold there is no photoelectric emission and the energy gained by electrons from photons is used in enhancing the electron temperature. As $\Lambda(\nu) \to \infty$ the $\beta(\nu)\Lambda(\nu)$ should be replaced by $[1 - \beta(\nu)]^{\Lambda(\nu)}$.

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Thus in this paper we only consider electrons for which $(E_x + h\nu) < W_a$ since only such electrons contribute to higher electron temperature and consequently higher thermionic current.

To understand the physics of enhanced electron emission we have analyzed the electron emission due to the incidence of white light radiation (concentrated sunlight) on the surface, which is relevant to space applications. Computations have been made for a cathode of zirconium (which has a high melting point and low work function) and anode of copper. It may be mentioned that contrary to common understanding the phenomenon [10–12] of light (with frequency below threshold) induced field emission has established that $\beta \neq 0$, even when the frequency of the incident radiation is below threshold.

2 Theory

2.1 Enhanced thermionic emission at high electron temperature

The energy distribution of electrons, incident on the surface $x = 0$ (from inside) per unit area per unit time is given by [13]:

$$\mathrm{d}^2 n = (A_0 T_e^2/e) F_D(\varepsilon_x + \varepsilon_t - \varepsilon_F)\mathrm{d}\varepsilon_x \mathrm{d}\varepsilon_t, \qquad (1a)$$

where $\varepsilon_x = (p_x^2/2m_e kT_e)$, $\varepsilon_t = (p_t^2/2m_e kT_e)$, $A_0 = 4\pi e m_e k^2/h^3$ $(= 120$ A cm^{-2} K$^{-2})$ is Richardson's constant, T_e is the temperature of electrons in the plate, e is the electronic charge, p_t is the transverse component of momentum, perpendicular to p_x, $F_D(\eta) = [1 + \exp(\eta)]^{-1}$, $\varepsilon_F = E_F/kT_e$, E_F is Fermi energy of the metal and k is Boltzmann's constant.

The thermionically emitted electrons correspond to $\varepsilon_x > w_a$ $(= W_a/kT_e$, where W_a is the height of the surface energy barrier); then,

$$F_D(\varepsilon_x + \varepsilon_t - \varepsilon_F) \approx \exp(-\varepsilon_x - \varepsilon_t + \varepsilon_F). \qquad (1b)$$

The thermionic current density, i.e., the number of thermionically emitted electrons n_{th} per unit time per unit area of emitting surface and the mean energy of such electrons just outside the surface is given by:

$$n_{\mathrm{th}} = \int_{w_a}^{\infty}\int_{0}^{\infty} \mathrm{d}^2 n, \qquad (2a)$$

and

$$\varepsilon_{\mathrm{th}} = E_{\mathrm{th}}/kT_e = \int_{w_a}^{\infty}\int_{0}^{\infty} (\varepsilon_x + \varepsilon_t - w_a)\mathrm{d}^2 n/n_{\mathrm{th}}, \qquad (2b)$$

where E_{th} is the electron energy of emitted electrons, just outside the surface. On substitution for $\mathrm{d}^2 n$ from equations (1a) and (1b) in the above equations and simplifying we obtain [13]:

$$n_{\mathrm{th}} = (A_0 T_e^2/e)\exp(-\Phi/kT_e), \qquad (3a)$$

$$\varepsilon_{\mathrm{th}} = E_{\mathrm{th}}/kT_{\mathrm{e}} = 2 \quad \text{at the surface and}$$
$$\varepsilon_{\mathrm{th}} = 2 - \upsilon \quad \text{far away from the surface,} \qquad (3b)$$

where $\upsilon = -eV/kT_e$ and V the electric potential of the surface is negative; $\Phi = W_a - E_F$ is the work function of the emitting surface. However it is seen that in general:

$$n_{\mathrm{th}} = (AT_e^2/e)\exp(-\Phi/kT_e), \qquad (3c)$$

where A is substantially different from the Richardson constant A_0. This is explained [7] by the fact that the work function Φ is temperature dependent and given by:

$$\Phi = \Phi_0 - \Phi_1 T_e, \qquad (4a)$$

where Φ_1 can be positive or negative; for Zr Φ_1 is positive. Thus,

$$n_{\mathrm{th}} = (AT_e^2/e)\exp(-\Phi_0/kT_e), \qquad (4b)$$

with

$$A = A_0 \exp(\Phi_1/kT_e) \quad \text{or} \quad \Phi_1 = k\ln(A/A_0). \qquad (4c)$$

Thus it is seen that the electron current is an increasing function of electron temperature.

2.2 Energy balance of electrons

The energy distribution of electrons, which are incident on the surface $x = 0$ (from inside) per unit area per unit time and have their normal energies enhanced by $h\nu$ is given by [13]:

$$\mathrm{d}^2 n = \beta(\nu)\Lambda(\nu)(A_0 T_e^2/e)F_D(\varepsilon_x + \varepsilon_t + \varepsilon_\nu - \varepsilon_F)\mathrm{d}\varepsilon_x \mathrm{d}\varepsilon_t, \qquad (5)$$

where $\varepsilon_\nu = h\nu/kT_e$, and $\beta(\nu)\Lambda(\nu)$ is the probability of the incident electron gaining the energy $h\nu$ of the photon per unit time. The units of β are cm^2 s.

An electron, incident on the surface and having its normal energy enhanced by $h\nu$ remains inside the plate when $\varepsilon_x + h\nu < w_a$; this in effect enhances the total energy of electrons inside the plate. The rate of energy enhancement E_a of the system of electrons per unit area is given by:

$$(E_a/h\nu) = \int_0^{w_a - h\nu}\int_0^{\infty} \mathrm{d}^2 n = \left\{\int_0^{\infty}\int_0^{\infty} \mathrm{d}^2 n - \int_{w_a - h\nu}^{\infty}\int_0^{\infty} \mathrm{d}^2 n\right\},$$

where $\mathrm{d}^2 n$ is given by equations (4a)–(4c). Thus,

$$E_a = [\beta(\nu)\Lambda(\nu)(A_0 T_e^2/e)][\psi(\varepsilon_\nu + \varepsilon_F) - \psi(\xi)]h\nu, \qquad (6a)$$

where $\psi(\xi) = \int_0^{\exp\xi} \eta^{-1}\ln[1+\eta]\mathrm{d}\eta$ and $\xi = (h\nu - \phi)/kT_e$.

The rate of loss of energy E_e by the electron system due to emission of electrons per unit area is given by:

$$E_e = [n_{\mathrm{th}}(\varepsilon_{\mathrm{th}} + w_a)]kT_e. \qquad (6b)$$

In unit time n_{th} electrons get transferred from the cathode to the anode and back to the cathode (with no change of potential energy). The rate of loss of energy E_c of the

electron system in the cathode per unit area, due to this process is given by:

$$E_c = n_{\rm th}[\bar{\varepsilon}(\text{cathode})kT_e - \bar{\varepsilon}(\text{anode})kT_a], \qquad (6c)$$

where T_a is the temperature of anode and $\bar{E} = \bar{\varepsilon}kT_e$ denotes the mean energy of electrons, which depends on the temperature T_e and Fermi energy; in fact,

$$\bar{\varepsilon} = \left\{ \int_0^\infty \varepsilon^{3/2} F_D[(\varepsilon - \varepsilon_F)]\mathrm{d}\varepsilon \Big/ \int_0^\infty \varepsilon^{1/2} F_D[(\varepsilon - \varepsilon_F)]\mathrm{d}\varepsilon \right\}. \qquad (6d)$$

Since the electrons are at a higher temperature than the lattice temperature T_0, they will transfer energy to the lattice, through collision with phonons; in the phenomenological model [14] acoustic phonons have a mass $M = kT_0/s^2$, where s is the velocity of sound in the material. The mean energy transfer per unit time by an electron is of the order of $\nu_e(m_e/M)[\bar{E}(T_e) - \gamma kT_0]$, where ν_e is the electron collision frequency (with phonons) and γ is determined from the condition that the mean energy transfer per electron is zero when $T_e = T_0$ or $\gamma = \bar{E}(T_0)/kT_0$.

Hence the rate of energy loss E_L by the electrons to the lattice per unit volume is given by:

$$E_L = n_e\nu_e(m_e s^2/kT_0)[\bar{E}(T_e) - \bar{E}(T_0)] = \{n_e\nu_e(m_e s^2/kT_0)[kT_e\bar{\varepsilon}(T_e) - kT_0\bar{\varepsilon}(T_0)]\}. \qquad (6e)$$

The electron temperature can be determined from the energy balance of electrons viz by the solution of the following equation:

$$E_M + E_a = E_e + E_C + (VE_L/S), \qquad (7)$$

where E_a, E_e, E_C and E_L are given by equations (6a), (6b), (6c) and (6e), respectively, V is the volume of the plate, S is the area of the electron emitting surface and E_M is the energy received by the electrons out of that needed to keep the plate at a temperature T_0.

In the absence of irradiation (i.e., $\Lambda(\nu) = 0$) in the steady state, $T_e = T_0$, $E_a = 0$ and $E_L = 0$. Hence the energy E_M received by electrons (out of that needed to maintain a constant temperature T_0 of the plate) per unit time per unit area is given by:

$$E_M = n_{\rm th}(T_e = T_0)\varepsilon_{\rm th}(T_e = T_0)kT_0 + n_{\rm th}(T_e = T_0) \times [kT_0\varepsilon(\text{cathode}, T = T_0) - kT_a\varepsilon(\text{anode}, T = T_a)]. \qquad (8)$$

When the incident radiation is characterized by $G(\nu)d\nu$ as the number of photons incident per unit area per unit time with frequencies between ν and $\nu + \mathrm{d}\nu$, equation (6a) gets modified to:

$$E_a' = \int_{\nu_1}^{\nu_0} [E_a/\Lambda(\nu)]G(\nu)\mathrm{d}\nu, \qquad (6a1)$$

where the upper parenthesis $'$ indicates, the incidence of white light, $G(\nu)$ tends to zero at $\nu \to \nu_1 (= \Phi/h)$ and $\nu \to \nu_0 (W_a/h\nu)$.

3 Data

3.1 Zirconium (Zr)

From equations (3c) and (4b) and the data [13] for thermionic emission from a Zr surface we have:

$$n_{\rm th} = [330/1.6 \times 10^{-19}]T_e^2 \exp(-\Phi_0/kT_e)\ \text{cm}^{-2}\ \text{K}^{-2} = 2.06 \times 10^{21} T_e^2 \exp(-\Phi_0/kT_e)\ \text{cm}^{-2}\ \text{K}^{-2},$$

where $\Phi_0 = 4.05$ eV and $\Phi_1 = k\ln(330/120) = 1.01k$. Thus $\Phi(T_e) = \Phi_0 - 1.01kT_e$, and $\Phi(T_e)/kT_e = \Phi_0/kT_e - 1.01$.

The electron density in a metal is given by:

$$n_e = \frac{\text{valency} \times \text{Avogadro's number} \times \text{density}}{\text{atomic weight}}.$$

For Zr the valency is 2, the atomic weight is 93 and the density [15] is 6.52 g cm^{-3}; thus $n_e = 8.60 \times 10^{22}$ cm^{-3}.

Fermi energy E_{F0} at 0 K is given by [7]:

$$E_{F0} = (h^2/8m_e)(3n_e/8\pi)^{2/3} = 1.783\ \text{eV}. \qquad (9a)$$

Fermi energy E_F at electron temperature T_e is given by [7]:

$$E_F = E_{F0}\{1 - (\pi^2/12)(kT_e/E_{F0})\}. \qquad (9b)$$

The mean energy of electrons is given by equation (6d).

The electron collision frequency may be evaluated from the relation:

$$1/\rho = e^2 n_e/m_e\nu_e, \qquad (10)$$

where ρ is the resistivity of Zr. With the resistivity [15] $\rho = 335 \times 10^{-6}\ \Omega$ cm and $n_e = 8.6 \times 10^{22}$ cm^{-3} as evaluated earlier $\nu_e = 8.1 \times 10^{13}$ s^{-1} at room temperature (300 K). The collision frequency at electron temperature T_e:

$$\nu_e(T_e) = \nu_e(\text{at } 300\text{ K})(T_e/300)^{1/2}. \qquad (11)$$

The speed of sound in Zr may be taken as [16] 3.8×10^5 cm s^{-1}.

3.2 Interaction of photons with Zr surface

3.2.1 Evaluation of β for Zr surface

The photoelectric efficiency of Zr, at room temperature for frequencies causing photoelectric emission can be expressed as [17]:

$$\chi = \chi_m(729/16)(\nu_0/\nu)^4(1 - (\nu_0/\nu))^2$$

where $\chi_m = 0.28$ and $\lambda_0 = 307$ nm [18].

From the relation:

$$\chi(\nu) = (A_0T_e^2/e)\beta(\nu)\psi(\xi),$$

$\beta(\nu)$ at room temperature can be evaluated from the data [18] for $\chi(\nu)$. However this method does not work, when $\nu < \nu_0$. For $\nu < \nu_0$, the parameter β for room temperature may be obtained from the data on light induced field emission [12], using the available theory [13] However, no such data for high temperatures (1600 K) and corresponding to Zr is available. Thus we are left without any clue to the value or order of β for conditions of interest to us.

3.3 Copper (Cu)

The Fermi energy and work function of Cu are 7 eV and 5.1 eV, respectively.

3.4 Solar radiation outside earth's atmosphere

It is of interest to consider the incidence of concentrated solar radiation on the emitting Zr plate, since concentrated solar radiation is the envisaged source of light at satellite altitudes.

We consider the normal incidence of solar radiation on the cathode at satellite altitudes. The number of photons $dn_{\rm inc}$ incident per unit area per unit time on the cathode, which have frequencies between ν and $\nu + {\rm d}\nu$ (and wavelength greater than 122.6 nm) is given by [17–20]:

$$dn_{\rm inc} = \alpha(r_s/r_d)^2(4\pi\nu^2/c^2)[\exp(h\nu/kT_S) - 1]^{-1}(h\nu)^{-1}{\rm d}\nu$$

$$= \alpha G(\nu){\rm d}\nu, \tag{12}$$

where α is the concentration ratio, $r_s = 6.96 \times 10^{10}$ cm is the radius of the sun, $r_d = 1.5 \times 10^{13}$ cm is the mean distance between sun and earth ($\approx$ 1 AU) $T_s = 5800$ K is the temperature of the surface of the sun and c is the speed of light in vacuum.

The radiation of wavelength below 122.6 nm can be approximated [17,20] by the incidence of 3.25×10^{11} α photons per cm^2 s (on the surface) having a wavelength 122.6 nm (Lyman α).

4 Numerical results and discussion

4.1 Computation

For a numerical appreciation of the phenomenon we explore thermionic emission from a Zr plate maintained at a temperature of 1200 K and irradiated normally by concentrated Sunlight. For monochromatic radiation, equation (7), after substitution for E_M, E_a, E_e, E_c and E_L from equations (8), (6a), (6b), (6c) and (6e) reduces to:

$$\beta(\nu)A(\nu) = X/Y, \tag{13a}$$

where

$$X = [n_{\rm th}(\varepsilon_{\rm th} + w_a)]kT_e + n_{\rm th}[\bar{\varepsilon}({\rm cathode})kT_e - \bar{\varepsilon}({\rm anode})kT_a]$$
$$+ (V/S)\{n_e\nu_e(m_e s^2/kT_0)[kT_e\bar{\varepsilon}(T_e) - kT_0\bar{\varepsilon}(T_0)]\}$$
$$- n_{\rm th}(T_e = T_0)\varepsilon_{\rm th}(T_e = T_0)kT_0 - n_{\rm th}(T_e = T_0)$$
$$\times [kT_0\varepsilon({\rm cathode}, T = T_0) - kT_a\varepsilon({\rm anode}, T = T_a)], \tag{13b}$$

and

$$Y = (A_0T_e^2/e)[\psi(\varepsilon_\nu + \varepsilon_F) - \psi(\xi)]h\nu. \tag{13c}$$

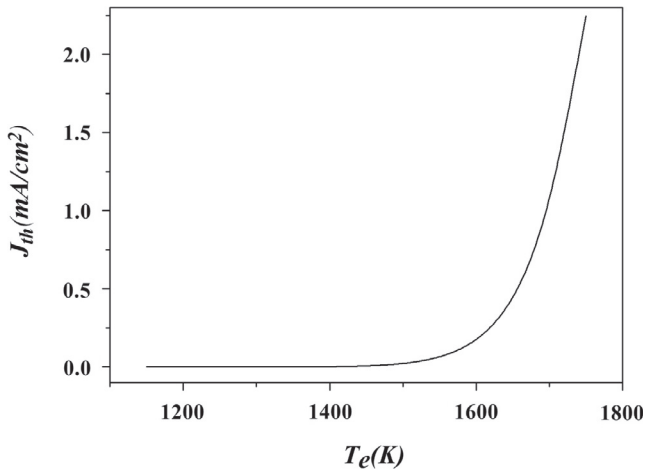

Fig. 1. Dependence of thermionic current $J_{\rm th}$ on electron temperature for a zirconium plate.

For concentrated sunlight at satellite altitudes, described by equation (12), equations (13a) and (13b) are valid but equation (13c) is replaced by:

$$Y = (A_0T_e^2/e)\alpha\int_{\nu_2}^{\nu_1}\beta(\nu)G(\nu)[\psi(\varepsilon_\nu + \varepsilon_F) - \psi(\xi)]h\nu{\rm d}\nu. \tag{13d}$$

Equation (13d) is obtained from equations (6a) and (6a1).

As explained before radiation with $\nu > \nu_0$ does not contribute to electron heating in the plate.

4.2 Results

The electron temperature may be obtained from the solution of equations (13a)–(13d). The corresponding emission current per unit area viz. $J_{\rm th} = en_{\rm th}$ may be determined from equation (4a).

4.2.1 Electron temperature and thermionic current per unit area

The variation of T_e and $J_{\rm th}$ correspond to a lattice temperature of 1200 K, well below the melting point of Zr.

Figure 1 illustrates the dependence of $J_{\rm th}$ on T_e, from which it is evident that only electron temperatures with $T_e > 1600$ K are of interest from the point of view of thermionic emission. Figure 2 displays the dependence of electron temperature and thermionic current from the plate on the concentration of solar radiation (at satellite altitudes). We have not considered the case $T_e > 1800$ K, because at such temperatures inelastic electron collisions with lattice are important and little is known about them. The following features of the effect of increasing the concentration ratio may be noted. The electron temperature with increasing intensity of concentration ratio of the radiation; this may be appreciated in terms of increasing number and total energy of electrons contributing to the rising temperature of electrons in the metal.

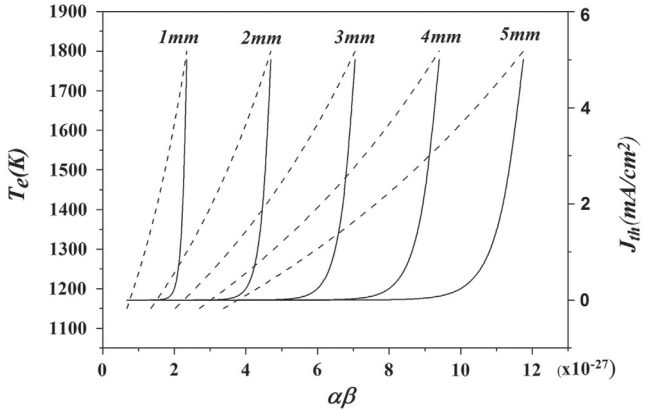

Fig. 2. Dependence of electron temperature and thermionic current from a zirconium plate, illuminated by concentrated solar radiation at satellite altitudes; α is the concentration ratio, $\beta(\nu)$ has been assumed to be independent of ν. The lattice temperature of the plate has been taken to be 1000 K. The solid lines refer to thermionic current per cm^2 while the broken lines correspond to electron temperature, for different thicknesses $V/S = 1$ mm, 2 mm, 3 mm, 4 mm and 5 mm.

1. The electron temperature (and thermionic current) decreases with increasing thickness of the plate. This is because the energy gain by the electrons is proportional to the surface while the loss to the lattice is proportional to the volume.
2. $J_{\rm th}$ rises very fast with increase in intensity of light concentration ratio beyond a certain value of the same; this may be appreciated by the fact that this critical value of α corresponds to the range of T_e where $J_{\rm th}$ varies very fast with increase in T_e (> nearly 1600 K); see Figure 1.

Thus it is seen that significant enhancement of thermionic current from an illuminated hot plate is obtained by incidence of light with frequency below threshold. The results are in terms of a parameter β, which cannot be estimated due to absence of data on high temperature light induced field emission for zirconium or for that matter any metal.

However using the available data [18] for at, we find that the photoelectric emission at high electron temperatures is negligible as compared to thermionic emission.

5 Conclusions

It is seen that significant enhancement of thermionic emission from a hot metallic plate occurs by incidence of light with frequency below the threshold. Following Fowler [8,9], some electrons hitting the surface from inside gain energy by absorption of a photon; these electrons are not emitted when the frequency of radiation is below threshold and these become part of the electron system, enhancing the electron temperature, which leads to enhanced thermionic emission. A scheme for the evaluation of the electron temperature and thermionic current is presented.

The results are of relevance to thermionic convertors operated in the mode, suggested by [6].

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