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Document No. ARA-1029

273533

CATALOGUE NO. STIA  
AS AD NO.

**SUMMARY REPORT NO. 1**  
**STUDY OF MATERIALS FOR THERMIONIC CONVERTERS**

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31 DECEMBER 1961

**OFFICE OF NAVAL RESEARCH**

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TASK No. NR 099-355

62-2 6

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Contract Nonr-3385(00)

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SUMMARY REPORT NO. 1

Study of Materials for Thermionic Converters

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Philip Goodman and Harold Homonoff

Allied Research Associates, Inc.  
Boston, Massachusetts

December 31, 1961

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## ABSTRACT

This program has been concerned with an examination of the fundamental properties of materials, from a solid-state physics and chemistry point of view, with regard to those properties which most influence their performance in thermionic converters. The underlying structural causes which determine the values of such material properties as work function, electron affinity, heat of vaporization, vapor pressure, thermal conductivity, Fermi level, etc. were examined for metals, insulators, and semiconductors with particular attention initially given to the true work function of alkaline earth oxides, transition metalloids (diborides, carbides, nitrides) and rare earth hexaborides, and the internal work function of semiconductors. Both quantitative calculations and qualitative correlations for various material classes are discussed. In connection with this study, a compilation was made of experimentally determined thermionic work functions and Richardson A values for most non-elemental emitters. Values for the band gap widths of nearly all semiconductors that have been found in the literature were also tabulated.

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## 1. Introduction

This investigation is concerned with the study and prediction of classes of materials, and of individual materials themselves, which show promise for utilization as one of the components of a thermionic energy converter. At the same time, it is concerned with the identification of those material classes which show little promise for such utilization.

The thermionic converter as a means of direct conversion of heat into electricity was first discussed many years ago (1). An emitter to which heat is supplied generates electrons which are received by a collector. Both the emitter and the collector are enclosed in an envelope which may be either evacuated or may contain a plasma, such as ionized cesium vapor. Although basically a very simple device, many problems have arisen because of the desirability of obtaining large power outputs from such converters. The electrons leaving an emitter tend to build up a space charge which retards the emission of subsequent electrons. One proposed method to reduce the effects of space charge involves the use of very close spacings between the emitter and collector. Another proposed method requires the presence of plasma; hence, the introduction of cesium vapor which, at the high temperatures present in the thermionic converter, becomes ionized.

The longevity required of useful thermionic converters has also resulted in the introduction of other problems associated with the necessity for use of extremely high temperatures. High temperatures are required because of the desirability of obtaining large currents and also because of the desirability of getting efficient conversion of heat into electricity.

Initially, this summary report will discuss some of the factors important to the attainment of high efficiencies in thermionic converters and those material properties that pertain to the performance of an operating converter. The remainder of the report is concerned with the thermionic work function of metals, insulators, and semiconductors, and with the various parameters that affect it in these solids.

Emphasis has been placed on the fundamental properties of materials from a solid state physics and chemistry point of view. An attempt has therefore been made to relate the thermionic work function of solids to various other parameters such Fermi level, band gap energy, electron affinity, impurity or defect levels, crystal structure and lattice spacing, orientation, electronegativity, lattice energy, type of bonding (metallic, ionic, or covalent), and surface properties.

## 2. Efficiency of a Thermionic Converter

The thermionic converter is basically a heat engine in which the thermodynamic efficiency is limited by the efficiency of a Carnot cycle. Thus, the higher the temperature of the heat input stage of the thermodynamic engine, the greater the efficiency which may be theoretically achieved, since this efficiency is, of course, a function of the difference in temperature between the input and output stage. But in a working engine, other loss factors are also introduced. The efficiency of a thermionic converter is defined as the ratio of the output power to the input power. Many authors (2-10) have formulated expressions for this efficiency and for the optimum operating conditions in a converter, taking into account the losses which are associated with both electrical and thermal factors. As a very general statement of the efficiency  $\eta$ , of such a converter, the expression

$$\eta = \frac{\phi_1 - \phi_2 - V_{\text{ext}}}{(\phi_1 + P_L / J)} \quad (1)$$

can be written, where  $\phi_1$  and  $\phi_2$  are the work functions of the emitter and collector respectively and  $J$  is the net current. All the thermal losses inherent in the operation of a thermionic converter are lumped together in  $P_L$ . Included in these losses are the radiative energy transfer from the emitter to the collector, the kinetic energy of the electrons which results in a rise of temperature of the collector, the thermal conduction through lead wires, and the gaseous heat conduction. The voltage drop in the external circuit,  $V_{\text{ext}}$ , determines the electrical loss resulting from the resistance of the electrical circuit. A compromise has to be reached in choosing the proper diameter of the leads to the external circuit since leads of small diameter would reduce the heat loss, but at the same time the effective voltage in equation (1) would be lowered because of the higher electrical resistance present.

In the case where  $P_L$  is the heat loss per unit area and consists wholly of radiation losses from the emitter and collector, the following equation pertains:

$$P_L = \sigma (T_1^4 - T_2^4) \left( \frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} - 1 \right)^{-1} \quad (2)$$

where

- $\sigma$  = Stefan-Boltzman constant,
- $\epsilon_1$  = Thermal emissivity of the emitter,
- $\epsilon_2$  = Thermal emissivity of the collector,

and  $T_1$  and  $T_2$  = operating temperatures of the emitter and collector respectively.

The saturation current,  $J_s$ , at a temperature,  $T^\circ K$ , generated from an electron emitter is given by the well known Richardson-Dushman equation

$$J_s = AT^2 \exp(-\phi_1 / kT) \quad (3)$$

where  $k$  is Boltzmann's constant and  $A$  is the Richardson  $A$  which has a theoretical value of 120 amps/cm<sup>2</sup>-deg<sup>2</sup>.

Hernquist (9) in treating the semi-ideal case substituted Equation (2) into Equation (1) and set the net current,  $J$ , equal to the saturated emission current of the emitter as given by Equation (3). The maximum efficiency then becomes

$$\eta = \left( 1 - \frac{\phi_2}{\phi_1} \right) \left[ 1 + \frac{\sigma}{A_1} \left( \frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} - 1 \right)^{-1} \frac{T_1^4 - T_2^4}{T_1^2} \phi_1^{-1} \exp(-\phi_1 / kT_1) \right]^{-1} \quad (4)$$

Thus it can be seen that a low collector work function and a low collector thermal emissivity favor higher conversion efficiencies. The efficiency is strongly dependent upon the work function of the emitter because  $\phi_1$  occurs in the exponential. In general, however, the efficiency at first increases with increasing  $\phi_1$  if the other quantities in equation (4) remain constant. It reaches a maximum for some value of  $\phi_1$  and then decreases for higher  $\phi_1$ .

Other more complex expressions for the maximum efficiency of a thermionic converter, in which most of the heat loss factors are taken into account, have been determined by Rasor (2), Houston (3), Hatsopoulos and Kaye (4), and Schock (5) among others. Most of these expressions were derived by assuming arbitrary but reasonable values for certain of the parameters and optimizing the efficiency equations with respect to various physical properties of the materials concerned such as dimensions and the thermal and electrical characteristics.

For example Rasor (2) derived a maximum efficiency equation in which the collector work function was arbitrary but the emitter work function and collector temperature were optimized. This is shown as

$$\eta_{\max} = \frac{\beta}{1 + 4E\phi_1^3} \quad (5)$$

where  $\phi_1$  is the emitter work function

$\beta$ , is a constant  $\approx 0.8$ , and

$$E = D\sigma\alpha^4 \frac{A_r \epsilon}{A_e J_s},$$

where  $D = 1 / (1 + 2k a/e)$  and is  $\approx 0.9$ ,

$k$ ,  $\sigma$ , and  $J_s$  have been previously defined,

$\alpha$  is a function of  $\phi_1$  and  $\phi_2$  and the temperatures which are chosen for the electrodes, and is approximately  $640^\circ\text{K}/\text{ev}$ . for the system considered by Rasor,

$A_r$  is the effective area for heat radiation from the emitter,

$A_e$  is the effective emitting area of the emitter,

and,  $\epsilon$  is the effective emissivity of the emitter-collector system.

Rasor has also attempted to derive a convenient figure of merit,  $M$ , for the thermionic converter as

$$M = \frac{1}{E\phi_1^3} = \frac{1}{D\sigma\alpha^4} \cdot \frac{A_e J_s}{A_r \epsilon \phi_1^3} \quad (6)$$

Converters of maximum conversion efficiencies greater than 16% are distinguished from those having lower efficiency by a value of  $M$  greater or less than unity, respectively.

By analogy with the figure of merit for a thermocouple, Hatsopoulos and Welsh (11) have obtained an expression for a quantity, suggested as a thermionic converter figure of merit, which includes terms representative of the properties of the emitter and collector, the conducting leads and their cross sections, the temperature and the space charge barrier.

### 3. Requirements for Materials for Thermionic Converters

Those material properties, both physical and chemical, which determine the performance of a given emitter or collector include the following:

#### a. The Work Function and Richardson A Value

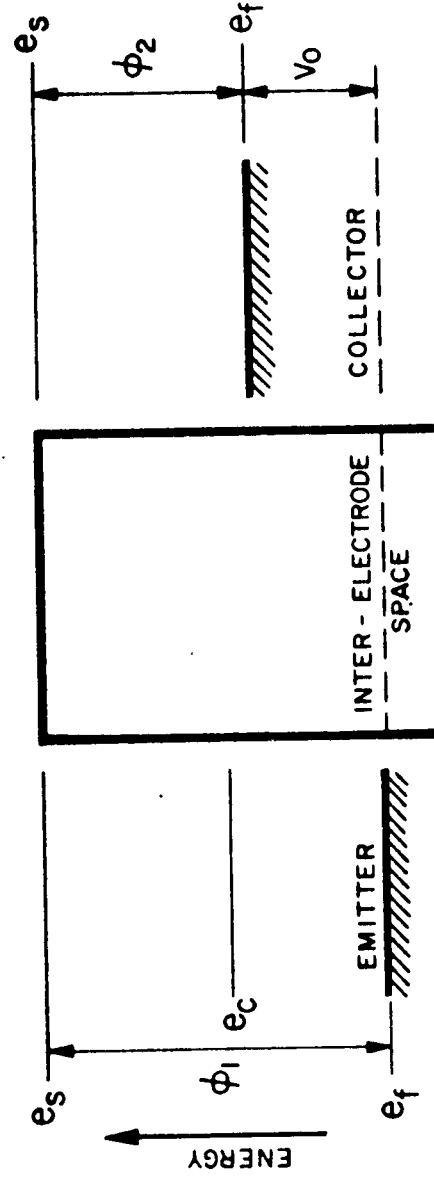
The output voltage of a thermionic converter is determined by the difference in the work function between the emitter and the collector, as is illustrated in Figure 1. Thus, the output voltage of a thermionic converter becomes greater as the difference between the work function of the emitter and the collector becomes greater. Hence, the emitter work function that is too low is undesirable. However, when operating at a given temperature, the output current is determined by the Richardson A and the work function according to Equation 3, and is reduced if  $\phi$  is too high or A is too low. At the same time, if back emission is to be avoided, the collector work function and A value should not be too low or high, respectively, and the temperature of the collector should be as low as possible.

#### b. Vapor Pressure and Rate of Vaporization

Although high emitter temperatures increase the theoretically attainable efficiency, these temperatures also introduce problems with respect to the vaporization of the emitter. Initially such vaporization alters the spacial configuration and hence the operating characteristics of the emitter. Eventually, the emitter itself disappears as an entity and the converter fails. Therefore, one prerequisite for a satisfactory emitter is a low vapor pressure at operating temperatures. For cesium vapor converters, the electrode spacing is in the order of a millimeter, and since a reasonable value for the allowed disappearance of material by vaporization can be approximated by requiring that the spacing shall not increase by more than 20% per year, a rate of surface recession that does not exceed about  $10^{-2}$  cm per year is required.

The rate at which a heated surface will recede due to evaporation of the material from the surface can be estimated using the Knudsen equation

$$Z = \frac{a P V}{(2\pi R M T)^{1/2}} \quad (7)$$



ENERGY DIAGRAM FOR THERMIONIC CONVERTER,  
 USING A SEMICONDUCTING TYPE EMITTER AND  
 NEGLECTING SPACE CHARGE EFFECTS

where Z is the rate of surface recession in cm/sec/cm<sup>2</sup> of surface, P is the equilibrium vapor pressure of the substance, R is the gas constant, M is the molecular weight of the substance in the gaseous state, V is the volume (cm<sup>3</sup>) per mole of the solid at the temperature of vaporization, T is the absolute temperature in °K, and a is the accommodation coefficient. Since the volume per mole of most solid substances which do not undergo phase transitions in the solid during heating does not change more than 5 to 7% from its value at room temperature to the melting temperature, the most important variable in the rate of surface recession is the equilibrium vapor pressure, P, of the solid which can be estimated from (12).

$$P = \left( \frac{2 \pi M k^2 \theta^2}{e L^2} \right)^{\frac{3}{2}} \frac{1}{\sqrt{kT}} e^{-L/RT} \quad (8)$$

where M is the mass of one molecule of the gas, k is the Boltzmann constant,  $\theta$  is the Debye temperature, which is directly proportional to the lattice vibrational frequency and which depends on the crystalline structure and the nature of the bonding between the atoms, e is the base of the natural logarithm. L is the molar heat of sublimation, and is the energy required to dissociate the solid into atoms or molecules at 0°K. It can be seen from Equation (8) that the vapor pressure is strongly dependent upon L. A more exact expression may be found in Tolman (13).

A reasonable approximation that would permit a surface recession rate of 10<sup>-2</sup> cm/year/cm<sup>2</sup> is estimated to be about 10<sup>-7</sup> mm Hg at operating emitter temperatures. Because the vaporization rate is dependent upon the molecular weight of the species being vaporized, and also upon the density and temperature of the solid, it cannot be unambiguously specified for all materials. This value that has been given for the maximum permissible vapor pressure is representative of that for a solid with a density of 4 gm/cm<sup>3</sup>, evaporating at 1900°K to yield a vapor with a molecular weight of 100.

One of the simplest optimization criteria which considers both work function and vaporization rate is that given by Wright (14), who proposed that a figure of merit for metallic emitters may be expressed as the ratio of the work function to

that temperature at which the vapor pressure is  $10^{-5}$  mm Hg. Zener et al (15) have set arbitrary limits with regard to the rates of vaporization of materials and the minimum permissible thermionic emission current. The resulting criteria have been applied to a number of elements and have led to the conclusion that no refractory element will serve the purpose of a long-lived thermionic converter emitter.

### c. Thermodynamic Stability

It is obvious that the materials used for the emitter and collector must be thermodynamically stable at the operating temperatures. If they were not stable, then the operating characteristics of the converter would change with time. This stability should exist not only with respect to decomposition of the particular chemical species present, but also should exist with respect to the particular crystalline phase that is initially present, since many materials are known to undergo phase changes at high temperatures only very slowly. For converters that are operated with a cesium vapor atmosphere, the thermodynamic stability of the emitter and collector materials must be such that free energy considerations do not favor reaction with the cesium vapor, other impurity gaseous species, or any solid substrates.

Parenthetically, it should be noted that cesium adsorbed on surfaces reduces the effective work function of the surface (16-18). Thus the presence of cesium in a thermionic converter makes a two-fold contribution to the performance since it also aids in reducing the space charge problem. However, during long-time exposure to high temperatures, it is conceivable that the cesium atoms may diffuse into the crystalline lattice of the emitter or collector. These diffusing cesium atoms must not exhibit a poisoning effect upon the thermionic emission and work function characteristics of the materials. Experimental studies of such potential poisoning do not appear to have been made except in conjunction with life-tests of cesium vapor thermionic converters.

#### d. Emissivity

For efficient conversion of energy the heat supplied to the emitter shall be used exclusively for the energy required to evaporate electrons. However, some of this energy will be reradiated by the emitter. The extent to which thermal energy is used for electron evaporation as opposed to being reradiated is determined by the emissivity of the emitter. The lower the emissivity, the smaller will be the energy loss resulting from reradiation. Radiant energy absorbed by the collector will raise its temperature, thus reducing the conversion efficiency. A low emissivity and a high reflectivity for the collector material is consequently also desirable.

Emissivities are functions of the temperature, the wave length, and the angle of observation. Any attempt to define classes of materials by means of characteristic emissivity values is quite difficult since materials exhibit emissivities that vary over large ranges of values and are dependent to a great extent upon the surface conditions. The only group of materials which exhibit some relationship between emissivities and other characteristic properties are the metals. Theories for estimating the emissivity of metals have been obtained from electromagnetic theory. Relationships using Maxwell's equations have been developed by Hagen and Rubens (19) for calculating the emissivity of metals,  $\epsilon$ , from their electrical resistance:

$$\begin{aligned} 0 < r_e T < 0.2 & \quad \epsilon = 0.751 \sqrt{r_e T} - 0.396 r_e T \\ 0.2 < r_e T < 0.5 & \quad \epsilon = 0.698 \sqrt{r_e T} - 0.266 r_e T \end{aligned} \tag{9}$$

where  $r_e$  is the electrical resistivity at T expressed in ohm-cm. Although the validity of these equations has not been established for any wave length regions other than the infrared, they have been used with some success in the shorter wave length regions.

Applying these relationships to alloys, it is found that to a good approximation, emissivities can be obtained using such relationships between emissivities and electrical resistivity, in an additive fashion from knowledge of the atomic

percent of each of the metals in the alloy. Comparisons of the calculated emissivities obtained in this fashion with measured emissivities have indicated an error that varies between 10 to 20% at the higher temperatures ( $\sim 2000^{\circ}\text{K}$ ). In addition, it was found that in those regions of the alloy where phase changes had occurred, changes also occurred in the emissive properties. This can probably be related to changes in the number and mobility of conduction electrons in the alloy.

#### e. Thermal Conductivity

This is another physical property which is of importance in thermionic converters especially in regards to the lead going to the external circuit. If the thermal conductivity of this lead is high, then thermal energy will be lost not only through radiation, but also by conduction through the lead.

Four separate modes of thermal energy transfer are considered pertinent for solid materials. These are heat conduction by thermoelastic lattice vibrations (phonons), conduction by free electrons moving in the solid, conduction by excited atoms (excitons), and energy transfer by the passage of electromagnetic radiation. The conductivity resulting from phonon and electron conduction are considered as being basic processes, while the other two are considered to be complementary energy transfer processes. Solid materials can be separated into two distinct classes which possess thermal conductivity properties peculiar to themselves - insulators and metals. The third class, semiconductors, possess characteristics of class 1 and 2 but since they are normally not very good conductors of electricity they show more pronounced insulator type thermal conductivity than metallic conductivity.

An expression for relating the phonon or electron thermal conductivity in a solid with certain other solid state phenomena such as the velocity of sound through the solid, the capacity for energy storage, and the various resistance mechanisms which affect the transfer of energy through the solid is often expressed in the following manner:

$$\delta = 1/3 \lambda \mu C \quad (10)$$

where  $\delta$  is the thermal conductivity due to phonon or electron transfer,  $\lambda$  is the mean free path for phonon and/or electron interactions and is a function of the scattering probabilities of the materials,  $\mu$  is the velocity of energy transfer and is assumed to be the velocity of sound within the solid, and  $C$  is the specific heat per unit volume which can be obtained from experiment, or from the Debye heat capacity function and the density.

In a hypothetical ideal crystal where there are no lattice defects and the lattice vibrations are harmonic, the mean free path for phonon travel can be very large, of the dimensions of the crystal. This would result in a thermal conductivity which is infinite. In real solids, however, the lattice vibrations are anharmonic and often lattice imperfections, grain boundaries, and impurities are present. All of these conditions cause scattering of the phonons, resulting in a reduced mean free path.

The total heat conductivity in metallic systems is generally considered to be composed of two main modes of energy transfer: electron conduction and lattice conduction. The magnitude of the lattice thermal conductivity, however, is insignificant in most pure metals which are good electrical conductors since the electronic contribution to the total thermal conductivity predominates. In metals which are poorer electronic conductors, the lattice conductivity can make a greater contribution to the total thermal transport and must be taken into consideration. The conductivity in metallic alloys is similar to the thermal conductivity in these poorly-conducting metals.

A thermal conductivity function for metals, which in a majority of cases exhibit very little temperature dependency, has been represented in terms of basic parameters by Klemens (20) as:

$$k_{\text{electron}} = \frac{2\theta u M k^2}{3 \pi \hbar^2} \left( \frac{\psi}{C_0} \frac{dE_f}{d\psi} \right)^2 \left( \frac{\psi}{q_0} \right)^2 \quad (11)$$

where  $k_{\text{electron}}$  is the conductivity due to electron transport (cal/cm sec  $^{\circ}\text{K}$ ),  
 $\psi$  is the magnitude of the electronic wave vector,  
 $E_f$  is the energy of the electrons at the Fermi level (ev),  
 $u$  is the velocity of the phonons (cm/sec),  
 $M$  is the average atomic mass (gm),  
 $\hbar$  is  $\frac{h}{2\pi}$

$C_o$  is a characteristic constant describing the coupling between the electrons and the lattice and has the dimensions of energy. For most metals  $C_o$  lies between 1 and 10 e.v.,  
 $q_o$  is the magnitude of the wave vector for phonons.

The use of Equation (11) as a means of predicting the thermal conductivity of a metal from its physical microstructure is limited since our knowledge of  $\psi$  and  $q_o$  is limited.

Difficulties which result from attempts to formulate a quantitative expression for lattice conduction in metallic materials can be partially attributed to the present status of experimentation in this area. Reliable methods for measuring lattice and electronic conductivity in metals and alloys have not been sufficiently developed. One method for obtaining the lattice conductivity has been to measure the electrical resistance and the total thermal conductivity. The electronic thermal conductivity,  $k_e$ , is then obtained from the Weidemann-Franz relationship:

$$k_e = LcT \quad (12)$$

where  $L$  is the Lorentz number,  $5.85 \times 10^{-9}$  cals - ohm/sec ( $^{\circ}\text{K}$ )<sup>2</sup>, and  $c$  is the electrical conductivity, ohm<sup>-1</sup> cm<sup>-1</sup>.

The lattice conductivity is obtained as the difference between the total thermal conductivity and the electronic thermal conductivity. This method assumes the validity of the Wiedemann-Franz equation and can only be used for those alloys or metals in which the lattice conducts an appreciable portion of the

thermal energy. In Figure 2, a comparison is made of the thermal conductivity of tungsten obtained in this manner, and that obtained from total thermal conductivity experiments (21). Another method by which the lattice thermal conductivity has been measured involves the effects of magnetic fields on electron conduction whereby the flow of electrons is suppressed by the magnetic field, and the thermal conductivity measured under these conditions is solely from phonon transfer.

At very high temperatures,  $> 2000^{\circ}\text{K}$ , thermal conductivity from radiation transport may also contribute substantially to the total thermal conductivity and at temperatures near  $4000^{\circ}\text{K}$  may be the dominant process for energy transfer. A comprehensive treatment of this phenomenon has been given by Chandrasehhar (21) and an equation relating certain factors was given by Hamaker (22) as:

$$K_{\text{radiative}} = \frac{8\sigma T^3}{a + 2s} \quad (13)$$

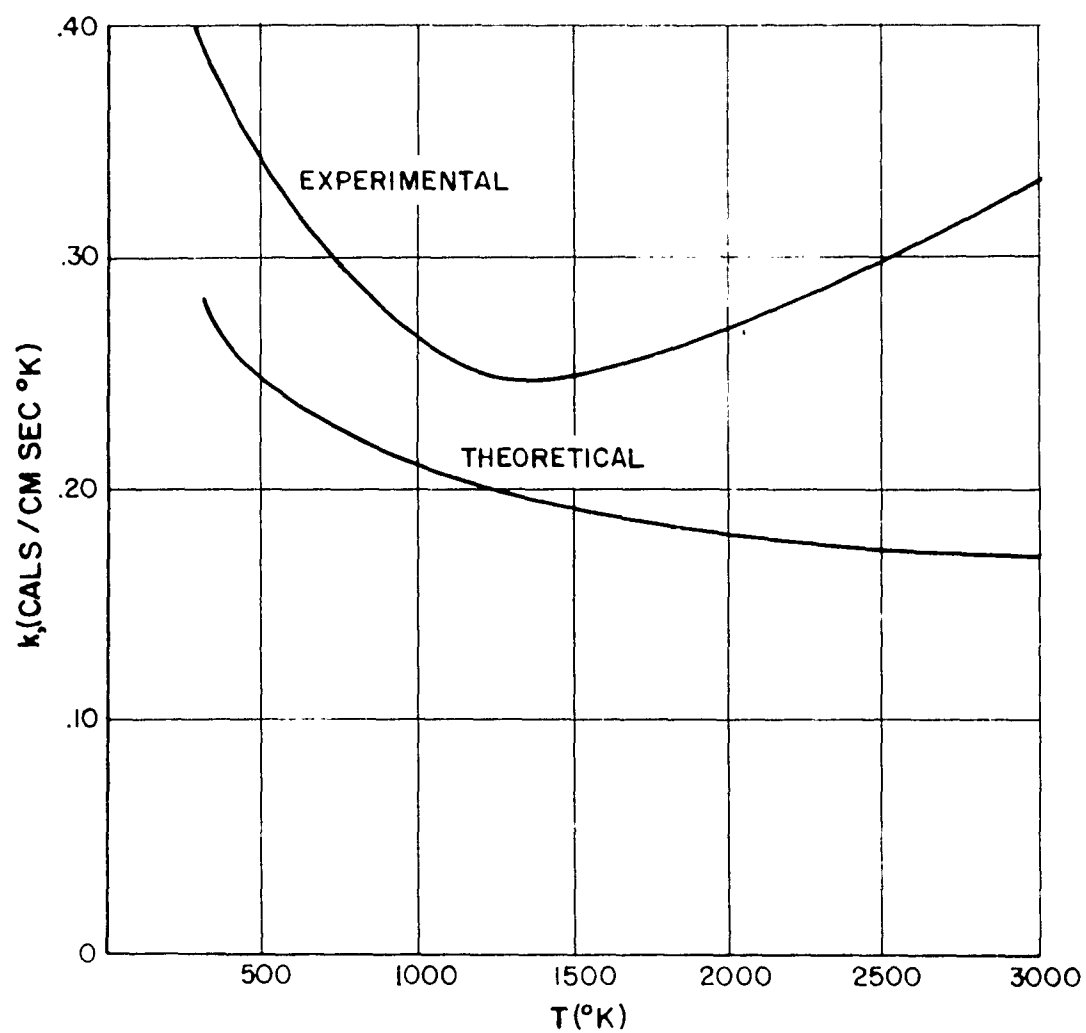
where  $a$  is the Hamaker absorption coefficient ( $\text{cm}^{-1}$ ),  
 $s$  is the Hamaker scattering coefficient ( $\text{cm}^{-1}$ ).

In Figure 2 the contribution of the radiative conductivity to the thermal conductivity can be seen in the high temperature region.

The thermal conductivity for crystalline insulators and semiconductors is frequently much more dependent on the temperature than is the case with metals and is found to decrease or increase with increasing temperature depending on which mode of heat transfer is predominant. Klemens (20) has indicated temperature variations for different scattering mechanisms. For semiconductors, especially at low temperatures, the total thermal conductivity is primarily attributed to lattice transport processes with the electronic thermal conductivity making more of a contribution at high temperatures. At very high temperatures, the contributions from the radiation and exciton thermal conductivity can be considerable and must be taken into consideration.

An equation which describes the lattice thermal conductivity of non-metals in terms of basic atomic parameters has been formulated by Leibfried and Schlomann (23) as:

COMPARISON OF THEORETICAL AND EXPERIMENTAL  
THERMAL CONDUCTIVITIES FOR TUNGSTEN  
AFTER SMITHELLS (21)



$$K_{\text{lattice}} = \frac{24}{10} \frac{(4)^{\frac{1}{3}}}{\gamma} \left(\frac{k}{h}\right)^3 m^3 \sqrt{V_a} \frac{\theta^3}{T} \quad (14)$$

where  $\gamma$  is Gruneisen's constant (dimensionless),  
 $m$  is the average mass of an atom (gm),  
 $V_a$  is the average volume of an atom ( $\text{cm}^3$ ).

In order for Equation (14) to be valid,  $T$  should be greater than the characteristic Debye temperature.

#### 4. Work Function - Definition

Of those factors which have been discussed as being important to the determination of the requisite properties of materials to be incorporated in thermionic converters, the one which is most critical is concerned with the thermionic emission of the materials. The emission is described by the Richardson-Dushman equation, Equation (3). Its presence or absence determines whether the converter works and the magnitude of the emission current determines the magnitude of the output current. Furthermore, differences between the work function of the emitter and collector determine the output voltage. It is thus profitable to examine more closely what can be predicted and what types of correlation are possible among various materials with regard to their thermionic emission. Since, in Equation (3), the exponential term is the one which largely determines the magnitude of the emission, the remainder of this paper will be devoted to a discussion of work function and of various attempts that have been made to predict and correlate work function for both elements and for compounds.

In recent years it has come to be recognized that there are at least three different types of work functions. The first work function, which is the one most clearly defined in terms of theoretical solid-state structure, is called the "true" work function. This work function is defined as the difference in energy between the Fermi energy within a material and the vacuum level outside the surface of the material. Some ambiguity remains in this definition, in that the vacuum level is not precisely defined. However, for most practical purposes, the differences are small between the energy of an electron located just outside the surface of an emitter and that of an electron at a large distance from the emitter. The second work function is the most practical definition of a work function. It has been termed the apparent work function, and is defined as the value obtained from the slope of a plot of Equation (3), i. e. a plot of  $\log J_s / T^2$  vs  $1/T$ . The third work function has been termed the effective work function and is obtained by a similar plot of Equation (3), but with the value of the constant A being taken as being the theoretical value,  $120 \text{ amps/cm}^2 \text{ deg}^2$ . Thus

values for two of these work functions are experimentally determined, those for the effective and for the apparent work function. The true work function, however, is basically a theoretical concept. The relations between these three work functions, their determinations and their implications have been discussed by several authors in recent years (see Hensley (25), Cusack (26), Nottingham (27), and Herring and Nichols (28)). The subsequent discussion concerning work functions of materials shall be essentially concerned only with the true work function. However, it must be emphasized that comparisons made between various materials on the basis of the experimental data must be made on the basis of experimentally determined work functions, which are not true work functions. In this sense at least, the comparisons will be in error. Other errors arise not only from experimental inaccuracies, but also because of the frequent lack of distinction in the literature between apparent and effective work function. The following discussions will be concerned with comparisons that can be made between work functions for a variety of materials, both elements and compounds. They shall not be concerned however, with such factors as patchy surfaces, mixed emitters, surface heterogeneities, grain size and porosity, or gross impurities.

The true work function may be expressed as the difference between two terms, both of which are referred to the energy level of the bottom of the conduction band in the solid (see Fig. 2). The first term,  $e_s - e_c$ , is called the electron affinity of the solid or the external work function. It is the energy difference between that of an electron at the surface of the solid and that of one at the bottom of the conduction band. The second term,  $e_c - e_f$ , sometimes termed the internal work function, is the difference between the energy of the electron at the bottom of the conduction band and its energy at the Fermi level within the solid. The sum of these two terms then is the true work function and is given by the equation

$$\phi_t = (e_s - e_c) + (e_c - e_f) \quad (15)$$

Because both the electron affinity and the Fermi energy are dependent upon temperature, the true work function is therefore dependent upon the temperature. The advantage of expressing the true work function as the sum of two terms lies in the fact that a degree of theoretical correlation and prediction is possible with regard to the variation of these two terms from molecule to molecule and as a function of the temperature, etc.

Frequently such comparisons have been made by assuming that one of these two quantities remains constant, and that the other quantity is responsible for the vast majority of the variations observed or predicted. The electron affinity of a solid is primarily a property of the structure of the solid and determined largely by the magnitude of the dipole layer of charge at the surface of the solid. As such, it is influenced by such factors as the interatomic spacings within the lattice of the crystals, such phase changes as may occur as the temperature is changed thus changing the interatomic spacing and the crystalline orientation, degree of cleanliness at the surface, patch effects etc. The Fermi energy is defined as the energy of that level within the crystalline electronic band structure which has an equal probability of being occupied or unoccupied at any given temperature. As such, it is a rather sensitive function of the electronic band structure within the crystal. Factors such as band gap energy, impurity or defect levels, and strength and type of bonding influence the Fermi energy. For extrinsic semiconductors it is also the quantity which is largely responsible for the temperature coefficient of the true work function, since in these materials, it is a function of the effective density of states which, in turn, are sensitive functions of temperature.

## 5. Work Function of Elements

Compilations of measured values of the work functions for the elements have been given by Michaelson (29) and Wright (14). Hermann and Wagener (30) have attempted to calculate the work function of a number of elements as a function of their crystalline lattice spacings. They first considered that either of two physical phenomena could be responsible for the origin of a potential barrier at the boundary of a metal and the vacuum in which it resides. One model supposed the existence of an electrical double layer at the boundary which was produced by the polarization of metal ions near the boundary caused by the inward direction of the electric field. The second model, and the one upon which their calculations were based, considered the image force which arises at the surface when an electron is emitted from a metal and induces a charge of equal but opposite magnitude in the interior. When this electron is at a finite distance,  $Z$ , from the surface the induced charge attracts the emitted electron with a force,  $F_i$ , that can be calculated from Coulomb's law and is known as the image force:

$$F_i = \frac{e^2}{4 \pi \epsilon_0 (2Z)^2} \quad (16)$$

where  $e$  is the electron charge,  $\epsilon_0$  is the vacuum dielectric constant,  $Z$  is the distance of the emitted electron from the surface. The field strength,  $E_i$ , which corresponds to this image force is

$$E_i = \frac{e}{16 \pi \epsilon_0 Z^2} \quad (17)$$

Schotky (31) calculated the absolute value of the image force potential  $V_i$  which is associated with the field strength, and is defined in such a manner that it approaches zero as  $Z$  goes towards infinity and gives an infinite potential for  $Z = 0$ . The equation for  $V_i$  is only valid for values of  $Z$  which are greater than zero and is given by

$$V_i = \int_{Z > 0}^{\infty} E_i \, dZ = \frac{-e}{16 \pi \epsilon_0 Z} \quad (18)$$

The shape of the potential curve as  $Z$  tends toward zero may be approximated, according to Schottky, by constructing a tangent from a point (where  $V_i$  equals the work function) on the ordinate axis to the potential curve which is represented by Equation (18). The potential is therefore considered linear from  $Z = 0$  to the tangential point  $Z = Z_0$  of this curve. The relationship between the work function and the critical distance was then derived by dividing the work function into two parts. The first of these parts refers to the distance  $Z = 0$  to  $Z = Z_0$  and is equal to  $E_i$  (Equation (17)) multiplied by the electronic charge,  $e$ , and by the distance  $Z_0$ . The second part, appropriate to the distance from  $Z_0$  to  $\infty$ , is determined by Equation (18) and equals  $\frac{e \cdot e}{16 \pi \epsilon_0 Z_0}$ .

The energy required to liberate an electron is thus the sum of these two parts and is given by

$$E_\phi = \frac{e^2}{8 \pi \epsilon_0 Z_0} \quad (19)$$

or

$$\phi = \frac{e}{8 \pi \epsilon_0 Z_0} = \frac{7.2 \times 10^{-10}}{Z_0} \quad (20)$$

where  $\phi$  is the thermionic work function and  $Z_0$  is in meters. The critical distance  $Z_0$  which defines the lower limit of the validity of Equation (18) for the image force potential is of the order of inter-atomic distances, i.e.,  $10^{-8}$  cm. because it is only within such a small distance that the image force potential is influenced by the interior of the metal concerned. Hermann and Wagener put  $Z_0$  equal to the lattice spacing,  $d$ , of the unit cell and considered that the value of the work functions obtained will be nearly proportional to  $\frac{1}{d}$ . This relationship appears to be valid only for the group 1A elements, i.e., the alkali metals.

Another method of calculating the work functions of elements which involves the theory of wave mechanics has been carried out by Tamm and Blochinzew (32) Mrowka and Recknagel (33), Bartelink (34) Hellmann and Kossatotschkin (35), Wigner and Bardeen (36), Bardeen (37), and Herring and Nichols (38). The methods used are based on a definition of work function as being the difference in energy between that of a metal lattice with an equal number of ions and electrons, and that of the lattice with the same number of ions, but with one electron removed. Wigner and Bardeen in 1935 (36) attempted to calculate the work functions of alkali metals by applying various modifications of metallic bonding theories originally proposed by Wigner and Seitz for calculating the energy of an uncharged metal (39). The work functions were found by first calculating the energy of the lattice containing  $N_i$  ions and  $N_e$  electrons. The final equations give the work functions of monovalent elements in terms of the heats of sublimation. The result is approximate and is considered to be valid only in a qualitative manner since one of the important factors, the electrostatic double layer of the surface, was omitted and calculations were based on the premise that the electrons were entirely free in the metal. However, Wigner and Bardeen did speculate that the dipole layers were due to the fact that the electron distribution is not as symmetric around the surface ions as is around the inner ones but is, rather, extended partially outside the limits of the surface ions. The double dipole layers are such that a constant potential is generated inside the metal but it varies outside. Wigner and Bardeen considered the value of the dipole moment to be  $< 1/2$  ev for the alkali metals. They also considered that the difference between the value of the work function for the various crystallographic planes of the same crystal, as observed experimentally, is determined by the difference in the dipole moments of the corresponding surfaces.

As indicated above, Wigner and Bardeen postulated that the work function of a metal consisted of two parts, the binding energy of the electron, and the energy required to move the electron through the electrostatic double layer at the surface. The first part can be calculated without reference to the surface.

The work function was defined by the equation:

$$-\phi = (\partial E(N_i, N_e) / \partial N_e) \quad N_i = N_e \quad (21)$$

$E(N_i, N_e)$  is the energy of the lattice and, using free electron values, depends upon the Fermi, Coulomb, exchange, and correlation energies of the metal.

The exchange energy per electron =  $\frac{0.458 e^2}{r_s}$ , where  $r_s = \frac{3 V_0}{4 \pi}^{1/3}$

and is the radius in Bohr units of a sphere whose volume equals the atomic volume ( $V_0$ ) of the metal under consideration. The Coulomb energy is defined as the classical electrostatic energy of the distribution of free electrons in each single atomic cell, approximated by that of a sphere of equal volume,  $\frac{0.6 e^2 x^2}{r_s}$ , where  $x$  is the number of valence electrons per atom.

The correlation energy is determined partially by utilizing a self-consistent field solution for electrons of the metal, which then is assumed to give essentially the same energy as that of a gas of free electrons moving in a constant external potential and possessing the same average electron density as is present in a metal. The assumption involved in the treatment appears to be valid for alkali metals in which the electronic structure consists of a single electron outside of completely filled shells. This treatment is certainly not valid for transition elements. The correlation energy is defined as the difference between the energy of the ground state of a metal and that of the self-consistent field solution and contributes to the total work function the quantity:

$$e^2 f(r_s) - \left( e^2 r_s f'(r_s) \right) / 3$$

where  $r_s f(r_s)$  is the Wigner correlation function (40). The maximum numerical value for the correlation energy was estimated by Wigner to be  $\frac{0.29 e^2}{r_s}$  in the case where  $N_i$  is assumed to equal  $N_e$ .

Another important energy parameter which must be taken into account in calculating the work function is the Fermi energy,  $E_f$ , which is taken as the mean kinetic energy of free electrons. Since the mean value of  $E$  must be taken over all the occupied states of electrons, the energy  $E_0$  of the lowest free electron level must be considered in addition to the Fermi energy. Also, since  $E_0$  can be expressed in terms of the ionization energy  $I$  and the heat of sublimation  $H$ , the final work function equation given by Wigner and Bardeen is:

$$\phi = I + H - \frac{2}{3} E_f - \frac{0.6e^2}{r_s} + 0.458 \frac{e^2}{3r_s} - e^2 r_s f'(r_s)/3 + eD \quad (22)$$

where  $D$  is the double layer moment at the surface of a metal at absolute zero and can be taken as  $4\pi$  times the dipole moment per unit area. Table 2 gives the work function of the alkali metals as calculated from Equation (22) using the assumption that  $D$  is zero.

In a later paper Bardeen (37) attempted to make a wave mechanical calculation of the electronic charge density at the surface of a metal in order to determine  $D$  and thus a more accurate estimation of the work function. The actual value of  $D$  was arrived at by first obtaining an approximate self-consistent solution of the Slater-Fock equations which include Coulomb and exchange potentials, and then introducing a "correlation potential" into the Schrodinger equation for each electron. A modified self-consistent field solution which was thus obtained yielded, for sodium, a value of 0.4 ev for  $eD$ . If the correlation terms are omitted,  $eD$  is 1 ev. Bardeen concluded that the surface barrier is determined primarily by the exchange and correlation forces, and that ordinary electrostatic interactions play only a minor role in alkali metals.

### a. Electronegativity vs. Work Function

Since rigorous theoretical calculations of the true work function for metals are not capable of predicting these values except perhaps in the simplest of metals, namely, the alkali and alkaline earth metals, it is therefore desirable to determine what types of correlations can be made with other more qualitative measures of chemical and physical binding of electrons within simple metals. One such correlation is that made by Gordy and Thomas (41) who related the work function of a number of metals to their electronegativity. The electronegativity is a chemical concept first introduced by Pauling (42) and currently used to characterize, in a qualitative fashion, the bonding that exists between unlike atoms in various types of molecules. Pauling originally set up his scale of electronegativity values on the basis of the equation.

$$(x_a - x_b) = 0.208 \Delta^2 \quad (23)$$

where  $x_a$  and  $x_b$  represents the electronegativity of the atoms a and b joined together in a chemical bond, and  $\Delta$  is the energy difference between that bond energy to be anticipated if a pure covalent bond were present between atoms a and b and the observed energy of the bond. The difference,  $\Delta$ , is attributed to ionic resonance energy. Thus, the scale of electronegativity is related to the attractive forces for a given element for electrons. Gordy (43) originally suggested that electronegativity values could be calculated from the equation,

$$x = (Z_{\text{eff}}) e/r \quad (24)$$

where  $Z_{\text{eff}}$  is the effective nuclear charge of the bonded atom upon the bonding electron when the electron is at a distance from the nucleus equal to the covalent radius  $r$ . The calculations for  $Z_{\text{eff}}$  take into account the screening effect by other electrons present in the unfilled valence shelves. In order to bring the values calculated from Equation (24) into accord with the Pauling scale, a proportionality constant and a shift in origin was required and resulted in

$$x = 0.31 \left( \frac{n+1}{r} \right) + 0.50 \quad (25)$$

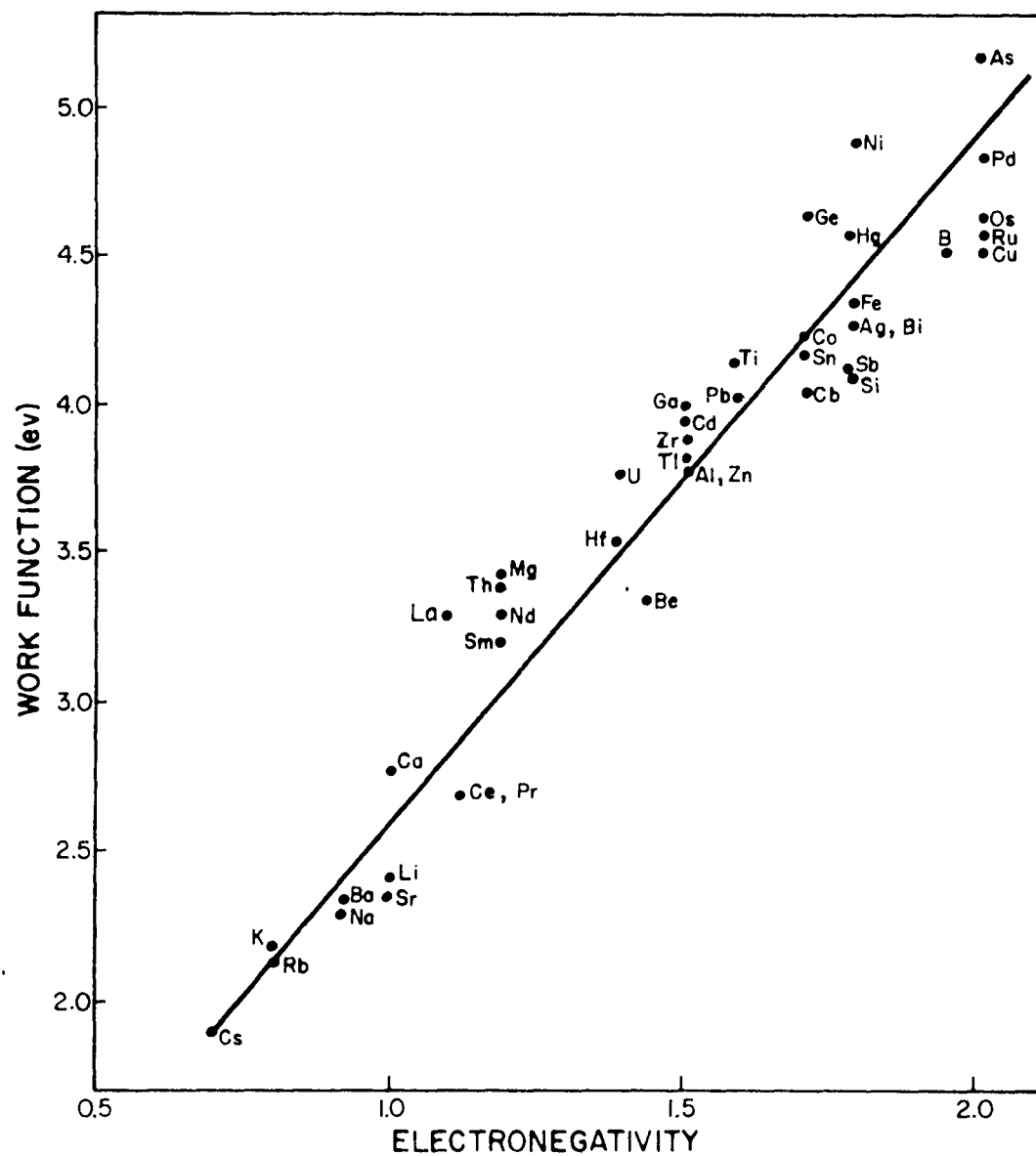
where  $n$  is the number of valence electrons. Still other methods of estimating electronegativity values have been proposed by Gordy (44) who related electronegativity to bond stretching force constants, bond lengths and bond orders; by Walsh (45) who related electronegativity to the stretching force constant of the elemental bond to hydrogen; and my Milliken (46) who proposed that the electronegativity of an element be determined by the arithmetic mean of its first ionization potential and its electron affinity.

The relationship shown by Gordy and Thomas between the work function and their electronegativities is reproduced in Figure 2. It may be seen that the smaller the electronegativity, the smaller the work function. The equation for the straight line shown in this figure is

$$x = 0.44 \phi - 0.15 \quad (26)$$

From the concept and formulation of the electronegativity values, it is evident that small electronegativity values are associated with small attractive forces between valence electrons and the effective nuclear charge. Probably the most fundamental parameters related to electronegativity are the interatomic force constant and the interatomic distances. However, these cannot be used directly since the values are modified by such factors as the coordination number of the element in the solid. Gordy's method (41) of calculating electronegativity values is reasonably satisfactory for simple elements. However, for transitional elements, there is difficulty with estimating the proper value to be assigned to the screening constants for those electrons located in unfilled inner orbitals.

WORK FUNCTION OF METAL VARIATION WITH  
ELECTRONEGATIVITY  
(AFTER GORDY AND THOMAS (41))



## 6. Work Function of Ionic Solids

Atomic structure and energy levels for isolated elements are reasonably well understood. When interatomic forces between elements must be considered, as in a solid metal, the computation of energy levels is more complicated and can only be done on an approximate basis. However, when elements chemically interact to form chemical compounds in the solid state, calculations become even more complicated, and approximate. One commonly used approximation involves the assignment of valence electrons to individual atomic orbitals, but there is no certainty with regard to this assignment within the solid compound. Once the assignment of electrons to atomic orbitals is made, the calculation of energy levels and band structure in the solid is just as approximate and difficult as it is for elemental solids. Some of the attempts that have been made to predict energy levels and true work functions of different types of compounds in the solid state are discussed below and in Section 7. In many cases, the fundamental quantities that are important for the determination of energy levels are also important for the determination of other properties which are of interest with respect to the use of materials in thermionic converters.

An ionic solid is probably the simplest solid compound to visualize. It consists of elements organized together in such a way that the electropositive element has donated one or more of its valence electrons to the electronegative element. It is probable that no real solid is truly ionic and that the bonding that exists within even the most ionic solid has some covalent character to it. Nevertheless, it is possible to treat many compounds as being essentially ionic. The alkali halides are considered to be the most ionic of the known compounds in the solid state, although even within this group there are wide variations in ionicity of the bonds. Various oxides and sulfides are generally also considered to be ionic and it is even conceivable that certain carbides and nitrides possess considerable ionic character. As pure compounds, ionic compounds are insulators. However, they can be converted into semi-conductors when interference (impurity or defect) levels are introduced into the crystal, thus disturbing the normal band structure of the insulator.

A method of computing the energy levels, the electron affinity and the probable maximum value for the work function of alkali halides has been developed by Mott and Gurney (47) and was subsequently modified by Wright (48). For the sodium chloride crystal, it was assumed that the single 3 s electron of the sodium atom has entered the 3 p quantum level of the chlorine atom, thereby completely filling the 3 p band. The 3 s band associated with the sodium atom, considered to have a higher energy than the 3 p band of the chlorine atom, becomes the conduction band in the crystal. It remains empty unless electrons from the filled 3 p band can be given enough energy to enter the higher 3 s band.

A cycle was postulated which involved removal of an ion from the crystal, conversion of the ion to an atom and replacement of the atom inside the crystalline lattice. The net result was to either add an electron to a positive ion or to remove one electron from a negative ion. Equations were developed for three quantities:  $-X$ , the work required to introduce an extra electron into the crystal at an energy corresponding to the bottom of the conduction band;  $\phi$ , the work required to extract an electron from the valence band; and  $\theta$ , the energy required to remove an electron from the valence band but leave it within the field of the positive hole that is generated in this band. These expressions for  $-X$ ,  $\phi$ , and  $\theta$  involve such fundamental crystalline quantities as,  $W_L$ , the lattice energy per ion pair,  $a$ , the Madelung constant of the crystal,  $I$ , the ionization potential of the electropositive atom, and  $E$ , the electron affinity of the electronegative atom. These equations are presented by Wright as:

$$-X = W_L - I + \omega_2 + P \quad (27)$$

$$\phi = W_L + E + \omega \quad (28)$$

$$\theta = (2a - 1) \frac{e^2}{r} + E - I + \omega_1 + P \quad (29)$$

$$\text{where } W_L = a \frac{e^2}{r} - R \quad (30)$$

r = interionic distance

e = electronic charge

R = total exchange interaction between a central ion and all of its neighbors.

P and P' are terms which represent the energy required to insert an atom into the lattice in a position which had been occupied by a smaller positive ion, and the energy involved with transfer of an electron from a neighboring ion, thus converting it into an atom. These terms were omitted in Equation (28) since an atom replaces a larger negative ion. The terms  $\omega$ ,  $\omega_1$ , and  $\omega_2$ , are polarization energies and occur when an electronic charge is removed from a negative ion site transferred from a negative ion to a positive ion, or added to a positive ion site respectively. Since the surrounding medium is thus polarized, potentials are produced at the site in question. Mott and Littleton (49) have given methods for calculating  $\omega_1$  and  $\omega_2$  while de Boer (50) considered  $\omega_1$  to be equivalent to

$$\omega_1 = 2.03 \frac{e^2}{r^4} (a_1 + a_2) \quad (31)$$

where  $a_1$  and  $a_2$  are the polarizabilities of the ions.

Mott and Gurney determined experimental values of  $(\phi - X)$  and  $\theta$  by means of ultraviolet absorption bands and from these results deduced a value of  $X \sim 5\text{eV}$  for NaCl. The location of the interference levels was quite difficult to obtain accurately by experimental methods and for this reason Mott and Gurney used an analogy whereby the excited electron (in the field of the positive hole) was considered to be in a medium of dielectric constant  $K_0$ . The force between charges, and the difference in energy levels were multiplied by  $1/K_0$  and  $1/K_0^2$ , respectively. Thus, if the energy difference between the interference level and the empty band is known for one crystal it can be approximated for others of known  $K_0$  since the difference is proportional to  $1/K_0^2$ . This reasoning can also serve to point out the relationship of dielectric constant to thermionic work function among ionic compounds provided that the width of the band gap does not differ greatly. An equation which indicates more accurately the distance in the gap between the interference level and the conduction band is given by Hermann and Wagener (30) as

$$X - \theta = \frac{2 \pi m^* e^4}{h^2 \epsilon_{\text{eff}}} = 13.4 \frac{1}{\epsilon_{\text{eff}}} \frac{m^*}{m} \quad (32)$$

where  $m^*$  denotes the effective mass of the electron in the crystal lattice,  $m$  is the rest mass of an electron, and  $\epsilon_{\text{eff}}$  is an effective dielectric constant which has a value intermediate between the static dielectric constant and that determined by optical wavelength.

Wright's contribution to the estimation of maximum work function and electron affinity in alkali halides is to introduce the concept of bandwidth. The allowable energy range within the bands in the alkali halides may be very large, but the distribution of states is such that only a few states are permitted at extremities of the energy range and the vast majority of the energy states are concentrated around the center of the band. The expressions representing the energies for the removal and insertion of electrons remain the same except for the insertion of terms ( $\Delta$  or  $\Delta'$ ) representing the energy difference between the bottom of the conduction band and the maximum density of electron states in this band and, similarly, between the top of the valence band and the energy associated with the maximum density of electron states within the valence band. Modern theory would probably relate these energies to the Fermi levels rather than to the position of the maximum of the density of electron states. The values deduced for  $\phi$  are closely related to the thermionic work function if the position of the Fermi level is not too distant from the top of the filled valence band.

The analysis of the energy levels within ionic solids was extended by Wright to divalent oxides and to zinc sulfide. The outer two s electrons of the electro-positive element are assumed to enter the p shell of the electronegative element, and together with the electrons already present within the p shell, to form a completely filled valence band. When the doubly charged positive ion is removed from the crystal the energy required is  $\frac{4ae^2}{r} - R$  and the addition of an electron requires the energy,  $-I_2$ , where  $I_2$  is the ionization potential for the second electron. Replacement in the crystal then involves the energy,  $\frac{2ae^2}{r} - R$ . The equations obtained are:

$$-(X - \Delta') = \frac{2ae^2}{r} - I_2 + \omega_2 + P \quad (33)$$

$$\phi + \Delta = \frac{2ae^2}{r} + E_2 + \omega \quad (34)$$

$$\theta = \frac{(4a - 1)e^2}{r} + E_2 - I_2 + \omega_1 + P' \quad (35)$$

Some experimental values of  $\Delta$  were determined by O' Bryan and Skinner (51) while values for  $\Delta'$  were found by Seitz (52). The more precise an estimation of  $\Delta$ , the more accurate will be the calculation of  $\phi$ . X was found to have a maximum value of 0.6 ev for BaO and a value not exceeding 1 ev for the other alkaline earth oxides. Wright, in a later article (14), considered that there will be a small increase in  $\Delta'$  in passing from BaO to BeO, but that this is probably not sufficient to prevent the trend in X from being similar to that in  $(X - \Delta')$ . The overall results point out the uncertainty of the value for X and of its contribution to the thermionic work function.

In Table 2 are given the values of the work function  $\phi$  for the alkaline earth oxides, which were calculated in the manner previously described. Also given in the last column of Table 2 are experimental values of the apparent or effective work functions, but it should be noted that the experimental  $\phi$  values have generally been measured for solids that contain some impurities or defects in the crystalline lattice and/or possess a contaminated surface. Thus the Fermi level and/or the electron affinity is changed and consequently the work function. Also given in Table 2 are values for various physical and chemical parameters. Trends in lattice spacing, lattice energy and the ionization potential of the metal atom can be clearly seen.

The trends of these physical and chemical parameters should be the same for the alkali metal oxides of Group I. These should be expected to show smaller work functions than are exhibited by the alkaline earth oxides because of the larger ionic radius and the smaller ionization potential of the alkali metals as compared with the alkaline earth metals. This prediction is verified by a comparison of the experimental work function for  $Cs_2O$ , 0.75 ev, and the work function of barium

oxide, approximately 1.5 ev. These values will be found listed in Table 3 which includes most of the experimental values of thermionic emission constants that have been published for solid compounds of interest. Many of the values pertaining to alkaline earth oxide emitters have been omitted, however, because of the large number of conflicting investigations conducted on these emitters during the last fifty years. Also missing from Table 3 are data on mixed and film type emitters.

## 7. Work Function of Metalloids

Another major group of materials which is sufficiently refractory for incorporation into thermionic converters can be classed under the heading of metalloids. The term refers to chemical compounds in the crystalline state in which the metalloid atoms are bonded together to form a continuous network extending throughout the crystal. A number of different metallic elements can be incorporated into the crystal which exhibits many properties similar to those of metals. The type of chemical bonding that exists between the metallic atoms and the network is not at all clear. In fact, it may be that a variety of bonding types exist within the various metalloids. Included among the groups of metalloids are such compounds as the borides, carbides, nitrides, beryllides, and silicides. Only for the borides have the thermionic emission characteristics for a relatively large number of the metalloid group been investigated. Despite the fact that uranium carbide and uranium carbide-zirconium carbide mixtures are presently considered to be among the most promising thermionic emitters, very few other carbides have been investigated, nor have many nitrides. No values for the work function for beryllides, or silicides appear to have been published. The discussion that follows will therefore be largely concerned with the borides. However, attention will be drawn to resemblances to other types of metalloids where appropriate and possible. As opposed to the semi-quantitative calculations for work function and other quantities closely related to work function made by Wigner and Bardeen (36) and by Herring and Nichols (38) for metals and by Mott and Gurney (47) and by Wright (48) for ionic solids, the treatment of the work function of metalloids has been attempted only on a purely qualitative basis, largely by Samsonov (69) and his co-workers.

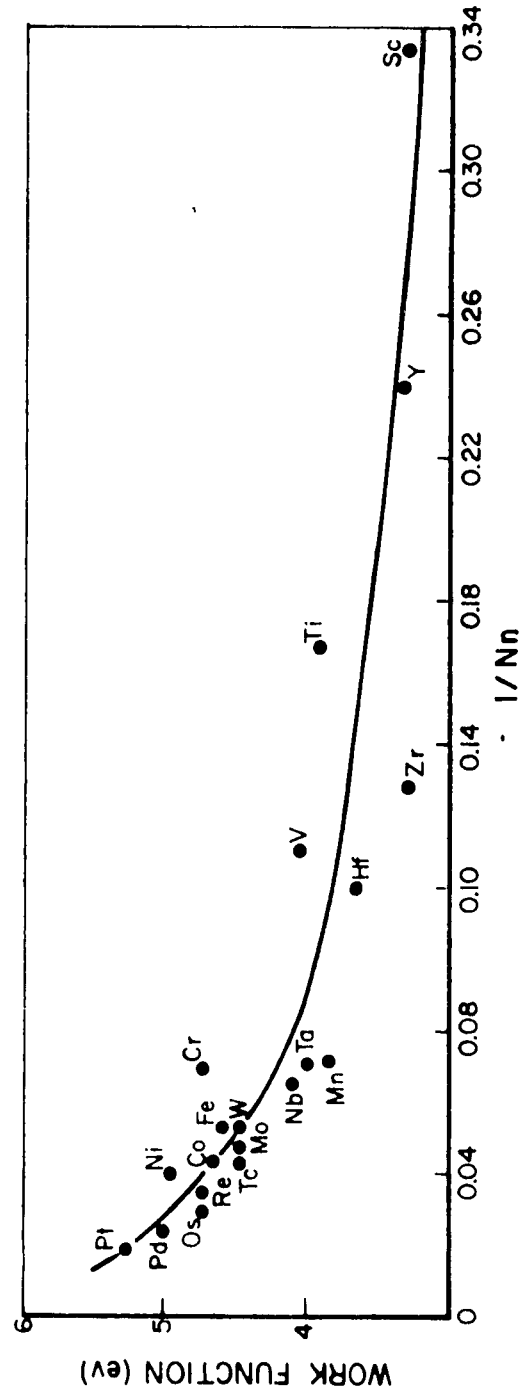
### a. Diborides

In attempting to relate a number of different physical, and especially electrical properties of solids containing transition elements, to their electronic structure, Samsonov (69, 84-91) has suggested the use of the quantity  $1/N_n$ , where  $N$  is the principle quantum number of the incomplete d shell of the transition

metal, and  $n$  is the number of electrons contained within this shell in the free metal atom. This quantity is considered to be indicative of the extent of the screening of the outer s electrons from the nuclear charge. Thus, the smaller the value of  $1/Nn$ , and the larger the value of  $Nn$  itself, the smaller is the attraction between the nucleus and the valence electrons. This quantity does not, however, take into account the particular stability of the half-filled d shell, nor does it consider the small difference in energy that exists between the d shell and the next higher s shell. Thus, Samsonov is required to make distinctions between the trends observed and predicted for groups IV, V, and VA compounds and the trends observable for groups VIIA and VIII. Comparisons cannot be extended because the considerations used by Samsonov primarily apply to the position of the Fermi level within the solid. The variations of the electron affinity of the solid with the structure and with the interatomic spacings present in the solid is not considered.

The assumption was made by Samsonov that the work function is a measure of the energy required to excite electrons from lower occupied levels in the conduction band to higher unoccupied levels within the same conduction band. He concluded that the work function for transition metals with large values of  $1/Nn$  should be smaller than the work function possessed by those metal with lower values. This was attributed to narrower bands being associated with the valence electrons because the electrons are held more tightly to the nucleus. The result is a smaller energy difference between the lower and upper states within the bands and the density of states on the Fermi surface was considered to be greater. The correlation between work function and  $1/Nn$  for transition metals is shown in Figure 4.

The bonding that exists within the transition metal diborides is not clearly established. The earlier theories of Samsonov (84-88) considered that the bonding between the metal and the nonmetal atoms in the structure was largely covalent, especially for groups IVA and VA. The electrons of both the nonmetal atoms and the metal atoms were considered to contribute to the electronic

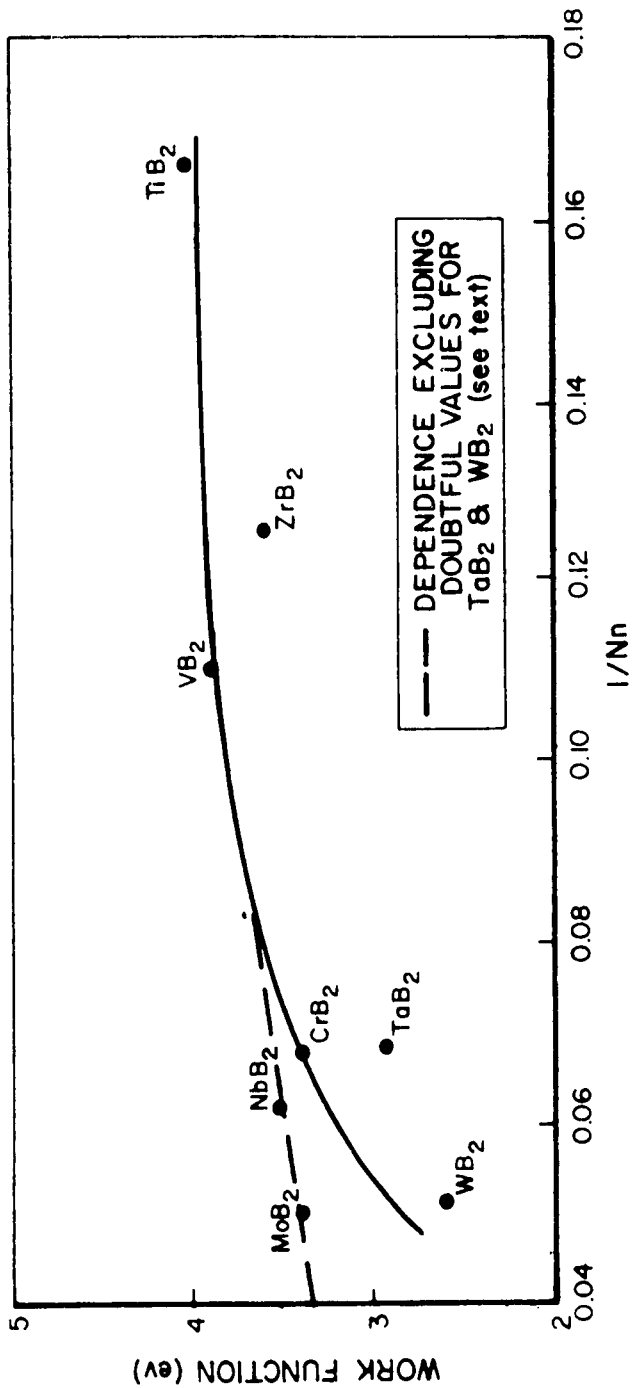


DEPENDENCE OF WORK FUNCTION OF TRANSITION METALS ON  $1/Nn$   
 AFTER SAMSONOV ET. AL (69)

collective, an s-d band in the crystalline lattice which is some type of unspecified hybridized orbital. The unused d orbitals remain empty and play the role of the electron acceptor while the two boron atoms per unit cell act as the donors. Despite the presence of strong covalent bonds in this picture, the metallic character of the compounds is maintained. For the diborides it is reasoned that an increase in the value of  $1/Nn$  for the transition metal atom is accompanied by an increased probability of transfer of the valence electrons from the boron atoms to the free, unoccupied levels in the s-d band. This results in a widening of the s-d band and, in accordance with the above reasoning, in an increase in the work function. The correlation obtained for transition diborides is shown in Figure 5.

In Figure 5, there is some question with regard to inclusion of the work functions for  $WB_2$  and  $TaB_2$ .  $W_2B_5$  is the only established stoichiometry, but there is some evidence that  $WB_2$  is the predominant phase at high temperatures (92). The stoichiometry of tantalum diboride is apparently  $TaB$  (66), and the crystalline structure is that of a face-centered cubic, NaCl-type structure, whereas the other diborides in Figure 5 possess simple hexagonal crystalline lattices. The method by which the work functions for most of the borides shown in Figure 5 was determined was not given, but it is thought that these are effective work functions. (Using the same experimental emission data, the effective work function will probably be higher than the apparent work function.)

The reasoning applied by Samsonov and co-workers to the prediction of values of work functions for diborides has been extended (69, 90) to provide a comparison between the work functions for corresponding transition metal borides, carbides and nitrides. Since the probability of transfer of valence electrons from the metalloid atom into the s-d band should vary with the inverse of the ionization potential of the metalloid atom, the higher the ionization potential, the narrower should be the s-d band and, as a result, the lower should be the work function. Consequently, the work function is predicted to decrease as one goes from borides to carbides to nitrides. The ionization potential of these metalloid atoms are 8.30, 11.26, and 14.54 ev., respectively. If this same reasoning were applied to the beryllides and silicides, whose ionization potentials are 9.32



DEPENDENCE OF WORK FUNCTION OF TRANSITION  
METAL DIBORIDES ON  $1/Nn$   
AFTER SAMSONOV ET. AL (69)

and 8.15 ev. respectively, then the silicides would be expected to have the highest work function whereas the beryllides should have a work function intermediate between that of the borides and the carbides.

The above view of the nature of the bonding orbitals in diborides is similar to that proposed by Rundle (93) and by Hume-Rothery (94). In order to get some idea of the band structure of the diborides, Juretschke and Steinitz (95) made a comprehensive study of the Hall coefficient and electrical resistivity of these compounds. They concluded that the band structure of the various transition metals is not drastically changed from that of the metal on combination with boron. They also considered the substitution of one transition metal for another changed mainly the number of electrons in the conduction band. Using Kiessling's speculations (96) that six electrons from the two boron atoms contained within each unit cell (electron configuration  $1s^2 2s^2 2p^1$ ) enter the d bands of the metal, Juretschke and Steinitz speculated that the energy of these bands are appreciably lower in the diborides than in the corresponding metal because the presence of interstitial borons tends to decrease the potential energy in the region between the transition metal atoms. They further speculate that the s-band is filled only to a very small extent in the fourth transition group ( $TiB_2$ ,  $ZrB_2$ ,  $HfB_2$ ) with additional metal electrons in the diborides of the fifth and sixth groups being accommodated mainly in this s-band. This picture is thus consistent with the trends in electrical properties and, according to Juretschke and Steinitz, also accounts for the decrease in cohesive energy (which influences the melting point) in going from group four to group six since the density of states in the conduction band is increasing at the same time. They also consider that group V and VI diborides are more likely to have imperfections and dislocations in their crystalline structures. Support for this hypothesis comes from the observation that these diborides may exist over a fairly large range of boron concentration on either side of the stoichiometric ratio. Still another cause for this decrease in cohesive energy may be the deviation from Hagg's rule that is found in group V and VI diborides. According to Hagg (92), metalloids can be classified as interstitial compounds when the metal atoms form a

three-dimensional framework which is similar to one of the typical atomic arrangements in an elementary metal. The nonmetal atoms are accommodated in the interstices of the metal skeleton. The type of interstice that is occupied by the nonmetals is determined by the radius ratio  $\frac{r(\text{nonmetal})}{r(\text{metal})}$  where the tetrahedral nonmetal radius and the 12 coordinated metal radius is used. When this ratio is between 0.41 and 0.59 (Hagg's rule), normal interstitial compounds of simple structures - cubic and hexagonal-are formed. At higher values of this ratio the structure becomes more complex although the metallic character of the compound may be retained. This increasing complexity is most noticeable in group VI where Hagg's ratio ranges from .60 to .69 and the existence of  $\text{MoB}_2$  and  $\text{WB}_2$  at room temperature is highly problematic.

Recently Samsonov (90) has apparently adopted the views of Juretschke and Steinitz in his explanation of various electrical and optical measurements for the diborides. This picture of the disposition of electrons within the bonding orbitals was suggested by, and is in conformity with, various electrical measurements which show that the group IV borides have higher Hall coefficients and lower electrical resistivities than do groups V and VI. The resultant greater electron mobility is attributed to an increase in the screening of the transition metal atoms by the filled d band which causes a decrease in electron scattering and hence, a higher electrical conductivity. Samsonov also points out that the idea of a filled d band agrees well with the absence of the long wave length line in the x-ray k-absorption spectrum for the group IV diborides.

Following the assumptions of Samsonov with regard to the relationship between the width of the conduction band and the work function, the widening of the conduction band as a result of the presence of electrons associated with the metalloid atoms in the d band can be interpreted to predict a higher work function for the Group IV diborides as compared with the work function of the pure transition metals. This prediction is borne out by the comparison of the work functions for  $\text{ZrB}_2$  and Zr, although no data exists for  $\text{HfB}_2$ , and the measured work functions for Ti and for  $\text{TiB}_2$  are the same. On the other hand, since the

Groups V and VI diborides possess electrons present in the s band, their work functions should be lower than that of the corresponding metal. Available data are in agreement with this conclusion. Applying similar reasoning to a comparison of the work functions for the diborides for groups IVA, VA and VIA, the resistivity is found to increase as the group number increases. If this increasing resistance is attributed to a narrowing conduction band, then still following Samsonov's reasoning, one would predict that the work function should decrease as one goes from Group IV to Group VI. The measured values of the work functions, as given by Samsonov (69), actually do follow this prediction.

Following this newer view, the resistivity of the transition metal carbides is greater than that of the borides because the d band in the carbides is not filled, and therefore, electron scattering does exist to a large extent. Since the conduction band in the carbides should be narrower than it is for the diborides, the work function of a carbide would be predicted to be lower than the work function for the corresponding diboride. Experimental data which exist confirm this prediction, but it should be noted that very few work functions for carbides have been determined and that, of those which have been measured, the accuracy is not very great.

Mention should be made of other property measurements that have been made by Samsonov and co-workers (98) on the transition metalloids. It was found that the values of the Seebeck coefficient,  $S$ , for the borides increased from approximately  $-10\text{uv}/^{\circ}\text{C}$  at room temperature to  $+20\text{uv}/^{\circ}\text{C}$  at  $1400^{\circ}\text{C}$ , the value for carbides decreased from  $-10$  to  $-30\text{uv}/^{\circ}\text{C}$  and for nitrides (TaN, TiN),  $S$  increased from  $-10$  to  $+5\text{uv}/^{\circ}\text{C}$ . These results are interpreted as indicating that hole conductivity may become important at higher temperatures in the case of borides and nitrides while for carbides, electron conduction predominates throughout the same temperature range. Larger values for the temperature coefficient of resistivity for  $\text{Mo}_2\text{B}_5$ ,  $\text{W}_2\text{B}_5$ , WC, TaN, and silicides

were found than for other transition compounds that were investigated. The values for borides in general are lower than those of corresponding carbides. According to Samsonov, the values are related to the rigidity of bonds in the crystal lattice with lower coefficients corresponding to stronger bonding. However, contrary to Samsonov, Juretschke and Steinitz (95) have found only a "small" resistivity dependence upon temperature for the group V and VI diborides.

The preceding discussion with regard to diborides is extremely qualitative and concerns itself largely with what, in more conventional terms, would be called the position of the Fermi level with respect to the bottom of the conduction band. It does not concern itself in any way with the electron affinity of the solid. In this connection, it is interesting to note that, although the diborides crystallize in hexagonal structures, most of the transition carbides crystallize in a NaCl-type cubic lattice. The hexagonal structure is not very different from a cubic lattice because the  $c/a$  ratio is almost unity. Nevertheless, the distinction between the lattice types makes it seem probable that the electron affinities of the carbides and borides cannot be equated.

#### b. Hexaborides

The alkaline earth and rare earth hexaborides have received considerable attention in recent years because of their relatively low work functions accompanied by their high temperature stability. The unit cell of a crystalline hexaboride is a body-centered cubic structure with each corner of the cube occupied by six boron atoms, positioned in such a way as to form a regular octahedron. These octahedra are located at the corners of a simple cube, in the center of which is a metal atom. Thus, the crystalline structure is that of two interpenetrating simple cubic lattices.

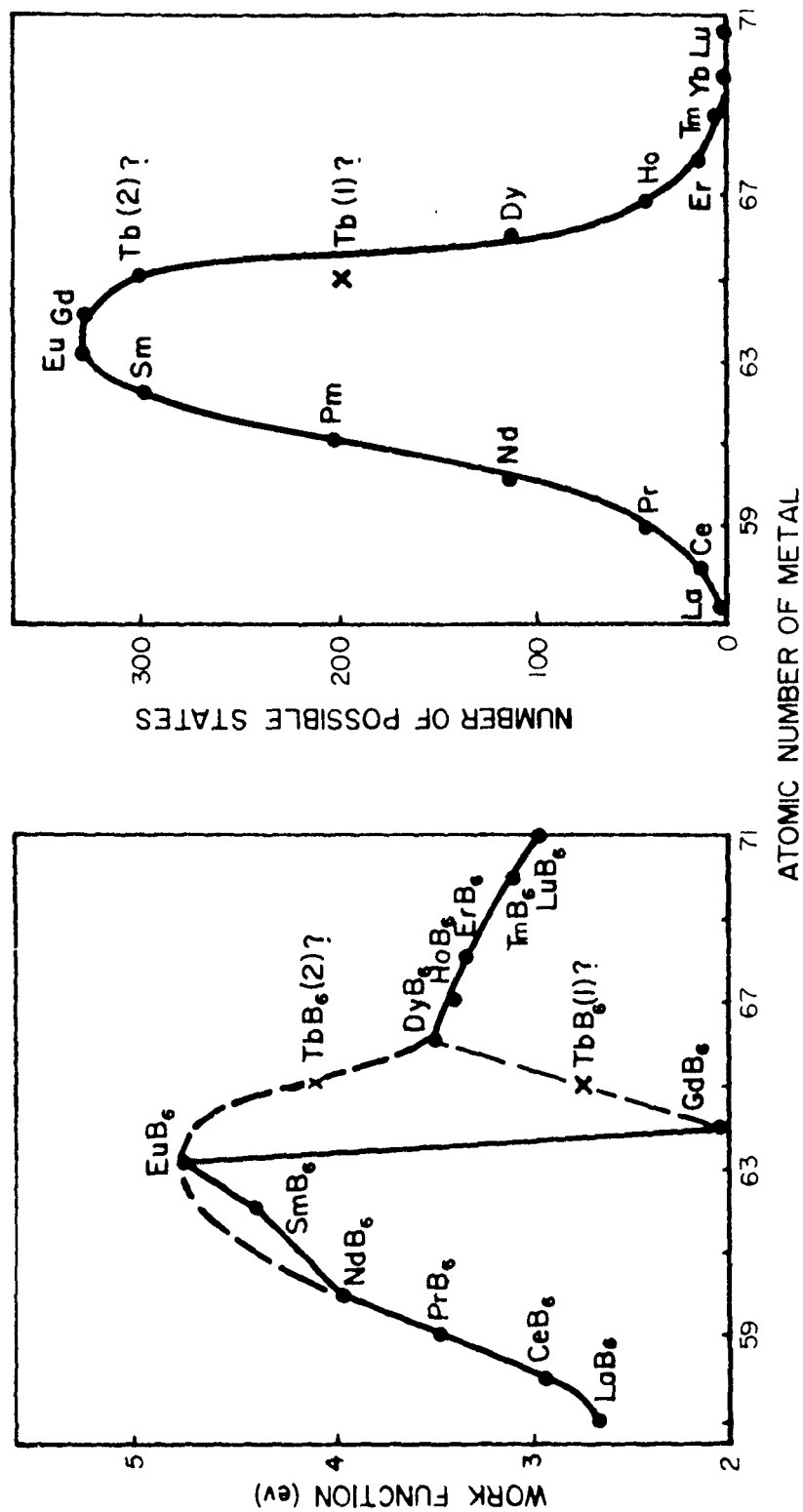
The hexaborides possess metallic properties and it is for this reason that Lafferty (71), during the course of his study of thermionic emission from hexaborides, postulated that each boron atom was bonded to five other boron atoms, and that the three valence electrons of the boron atom were distributed over

these five covalent B-B bonds. But no valence bonds were assumed to exist between the metal atoms and any of the surrounding boron atoms. This structure permitted the outer valence electrons of the metal atoms to remain associated with the metal and thus become contributors to a metallic type conduction.

An almost completely opposing point of view was adopted by Longuet-Higgins and Roberts (99), who made a quantum mechanical calculation of the bonding orbitals used for the hexaborides. They assumed that all the valence electrons of both the metal and boron atoms were confined to the boron network, which is equivalent to neglecting all structures involving covalent metal-boron bonds. This approximation becomes more valid as a difference in electronegativity between the metal and the boron atoms becomes greater and the bond approximates that of an ionic bond. The band structure, resulting from the LCAO molecular orbital approximation applied by Longuet-Higgins and Roberts, predicted a valence band capable of containing twenty electrons, eighteen of which would be contributed by the six boron atoms plus another two from the divalent metal atom. As a result of this calculation, they concluded that divalent metal hexaborides should be insulators and that any conduction observed for them is the result of impurities or lattice defects. However, the extra valence electron present in trivalent metal hexaborides is assumed by Longuet-Higgins and Roberts to be associated with the metal atom itself. In this case, the crystal should act as a metallic conductor.

This latter view of Longuet-Higgins and Roberts is essentially the same as that adopted by Neshpor and Samsonov (100). However, they permit the insertion, within the boron octahedron, of between 1.6 and 2 electrons from the metal atoms. The evidence for the insertion of less than two electrons from a divalent metal comes from the work of Bertaut and Blum (101), who replaced some of the metal atoms in the hexaboride with monovalent sodium atoms, forming compounds of the type  $(\text{Na}, \text{M})\text{B}_6$ . The limit of their substitution corresponded to 1.6 electrons per metal atom. The remaining 0.4 electrons per divalent metal atom, and 1.4 electrons per trivalent metal atom, remain

associated with the metal atom and are responsible for the metallic-type conduction of the hexaborides. For the rare earth hexaborides, Neshpor and Samsonov consider that the energy band system is composed of "a narrow, weakly-excited  $4f$  band," presumably the valence band, and "a broad, hybrid  $5d - 6s$  band." The latter band is considered to determine both electrical conductivity and the work function of a rare earth hexaboride. The work functions have been plotted as in Figure 6, wherein is also shown a plot given by Neshpor and Samsonov of the number of possible states that exist for the particular rare earth element. The assumption is made that Hund's rule, relating the degree of stability of an element to the multiplicity, is applicable to this particular electronic structure. Although the method by which the number of possible states for the  $4f$  electrons has been calculated is unclear, it is true that greater stability in rare earth elements is associated with the presence of a half-filled shell, as in Eu and Gd, both of which possess in their normal states seven electrons in the  $4f$  shell. The asymmetry of the work function versus atomic number curve is explained by the high degree of screening present in the higher atomic number rare earth hexaborides, which results in an increase in the work function according to the discussion given above for the diborides. Therefore, the decrease in work function on the right-hand side of Figure 6 is less rapid than is the rise in work function on the left-hand side. Gadolinium hexaboride has a low work function which is attributed to the presence of a single  $5d$  electron in the electronic configuration of the element. This  $5d$  electron is considered to be substantially free and thus results in a small work function for the compound. There are two possible electronic configurations for Tb:  $4f^8 5d^1 6s^2$  or  $4f^9 6s^2$ . Corresponding to these two possible electronic configurations, a work function between 2.06 and 3.53 ev or between 3.53 and 4.9 ev is predicted. An approximate value for this work function is 6.0 ev (76). Although the accuracy of this work function measurement is not very great. It is probably sufficient to indicate that the latter configuration of Tb is the correct one if the assumptions of Neshpor and Samonov are considered to be completely valid.



VARIATION WITH ATOMIC NUMBER OF WORK FUNCTION  
AND NUMBER OF POSSIBLE STATES FOR RARE EARTH  
HEXABORIDES

AFTER SAMSONOV AND NESHPOR (100)

## 8. Internal and External Work Functions of Semiconductors

Insulators and semiconductors, classes of solids which are of interest as materials in thermionic converters, show a range of chemical bonding from highly ionic to highly covalent. In Section 4 it was shown that the total thermionic work function of a semiconductor can be separated into an internal work function and an external work function, or the electron affinity. Data which have been published in the open literature pertaining to the electron affinity of compounds are quite limited, but indicate that ionic materials of large band gap have low electron affinity, i. e.,  $\sim 1$  ev. or less. Included among these materials are the alkali halides and alkaline earth oxides. The internal work function is related to the band gap energy which in turn, is influenced by the nature of the chemical bonding present. Thus, it is desirable to be able to predict the type of bonding which the many known semiconductors and possible new ones may possess and to also predict the chemical and physical properties which can be expected from these solids on the basis of their bonding characteristics.

The general rules for compound formation have been discussed by many authors (102-4) and have considered parameters such as electronegativity, atomic number, position on the periodic table, atomic radii, crystal structure, electronic configuration etc. Atoms in a solid may be packed in one of a limited number of symmetrical arrangements. In general, in going from compounds with mostly ionic bonding to those with mostly covalent bonding, the crystal structure, especially in simple MX compounds, ranges from the sodium chloride or cesium chloride structure to the wurtzite, zincblende, and finally the diamond-type structure. Compounds synthesized from elements of groups IA, IIA, or IIIA with VB, VIB, or VIIB tend to form ionic compounds of the NaCl structure. The exceptions are compounds such as BeO, BeS, BeTe, and MgTe which have a wurtzite or zincblende structure. MX compounds formed strictly from elements appearing on the non-transition element side of an extended (long form) periodic table, such as AlSb or SiC, generally have a greater degree of covalency than those formed when M is an element appearing in a subgroup A and X is an element appearing in a subgroup B.

In addition to the above conditions, additional parameters favoring ionic bond formation include, for the positive ion, large radius, efficient shielding by the inner electrons with a resultant low effective nuclear charge and a stable configuration of completely filled electronic shells in the ion. In an analogous manner, a negative ion should have a small radius, large effective nuclear charge, and a stable configuration. Pauling (42) has given an expression for the ionic character of a bond in terms of  $(x_a - x_b)$ , the difference in electronegativity of the two atoms which form the bond:

$$\text{Fraction of ionic character} = 1 - \exp \left[ -\frac{1}{4} (x_a - x_b)^2 \right] \quad (36)$$

Another method of estimating the amount of ionic character of a compound was derived by Szigeti (105). The static dielectric constant,  $k_o$ , was related to various other parameters such as the dielectric constant at high frequencies,  $k_\infty$ , the number of ion pairs per unit of volume, the mass of ions, and the frequencies of transverse lattice vibrations (reststrahlen). Also included in this expression is the parameter,  $S$ , which, when it departs from unity, is indicative of polarization effects resulting from short range nonelectrostatic forces and from non-spherical charge distribution on the ions. Other effects which can cause  $S$  to depart from unity are overlapping of ions and ionic charges of less than nominal value. As such, the departure of  $S$  from unity is indicative of the covalency present in the crystal and can be estimated from

$$S^2 = \frac{3.4 (k_o - k_\infty) M_1' M_2'}{Z^2 \frac{k_\infty + 2}{3} \lambda_t^2 \rho} \quad (37)$$

where  $M_1'$  and  $M_2'$  are the atomic masses,

$\rho$  is the density,

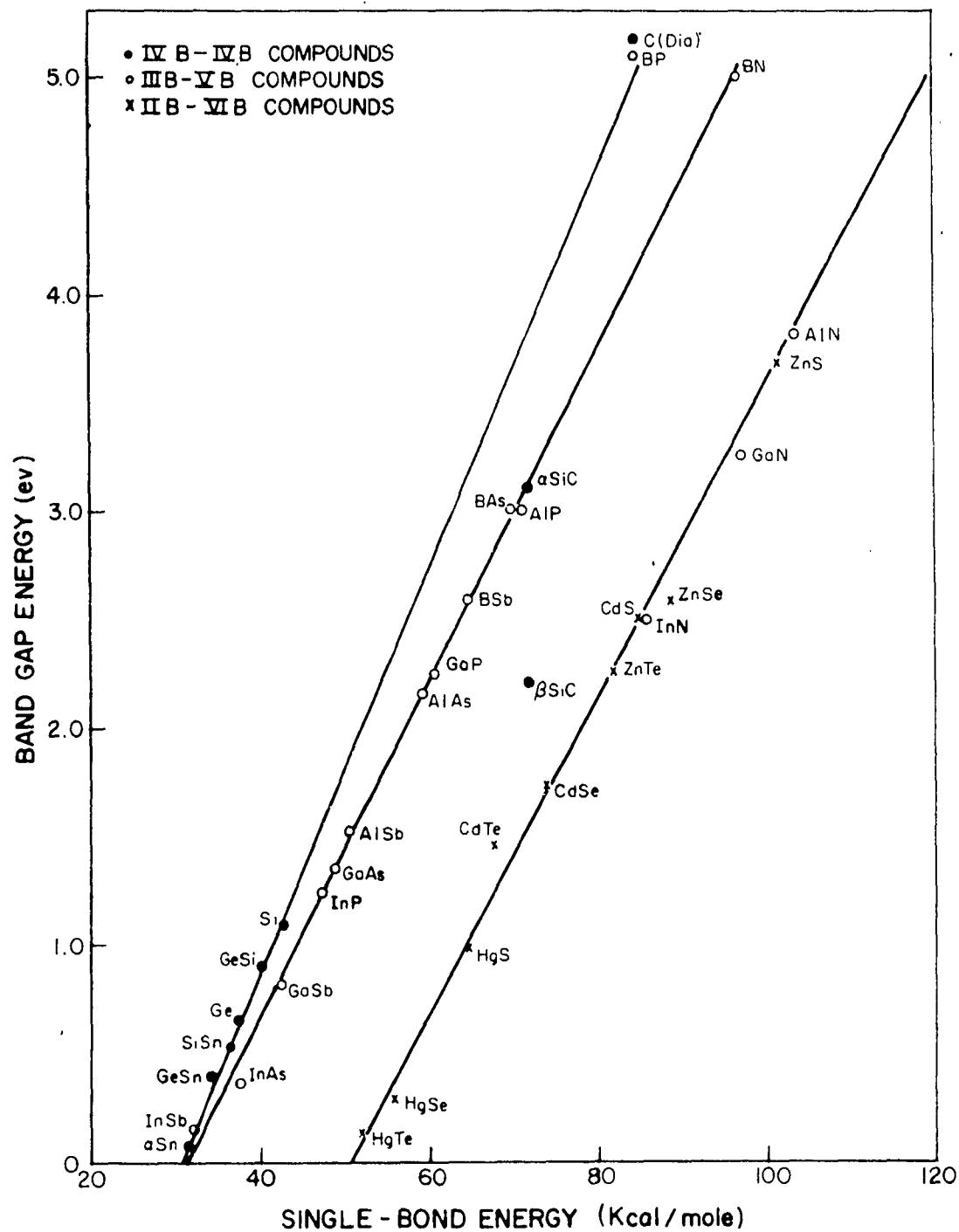
$Z$  is the valence,

and  $\lambda_t$  is the reststrahlen wave length in microns.

To date, values for  $S$  have been determined for only a few compounds, since the necessary dielectric constants and reststrahlen frequency are not known for most compounds. Among those compounds for which  $S$  has been determined are  $MgO$ ,  $ZnO$ ,  $ZnS$  with values of 1.0, 0.63 and 0.48 respectively. As a comparison, the amount of ionic character in these solids calculated from Equation (36) are 79%, 63%, and 22% respectively.

The only basic semiconductor property of primary interest in connection with work function which is known for a large number of materials is the magnitude of the band gap which is also related to the nature of the chemical bond. However, many of these values can only be considered approximate because of such factors as lack of complete knowledge of the particular optical absorption process used to measure the band gap and the uncertainties with regard to sample purity. Optical measurements of the band gap can differ from those obtained from thermal measurements because of the Franck-Condon effects which permit the optical determination to be larger than the thermal measurement, particularly for ionic solids. Accurate predictions of the width of the band gap is not yet possible, but useful empirical relations can be found between band gaps and such parameters such as bonding character, energy and interatomic distance. Table 4 gives values of band gaps for various solids. A number of trends have been observed, especially in substances with similar electronic and crystal structures. One important observation is that, with only a few exceptions, an homologous series of semiconductors with a similar degree of covalent bonding and the same crystal structure has a band gap energy which decreases with decreasing bond strength (106-8). An example of this is shown in Figure 7 for the group IVB-IVB semiconductors (which in one of their crystalline configurations possess a diamond-type structure) for which the bond strength continually decreases in going from diamond to  $\alpha$ -Sn. At the same time, the band gap energy decreases from 5.2 ev. for diamond, which is an insulator, to 0.08 ev. for  $\alpha$ -Sn, which is nearly metallic. Pb, which would be at the bottom of the series, has no band gap and is a metal. A similar relationship can be seen for groups IIIB-VB and IIB-VIB which are also plotted in Figure 7. Related properties such as interatomic distance, elastic constant, melting point and the Debye temperature tend to

### DEPENDENCE OF THE BAND GAP ENERGY ON THE SINGLE-BOND ENERGY



follow the same order (106). Burstein and Egli (106) and Lander (107) considered that the influence of ionic and covalent character on band gap width can be seen in various isoelectronic series of the wurtzite, zincblende or diamond-type structure. Several series which were analyzed are (a) CuBr, ZnSe, GaAs and Ge where the gap energy ranges continuously from  $\sim 5$  ev. for the more ionic CuBr to 0.6 ev. for the highly covalent Ge, and (b) AgI, CdTe, InSb and  $\alpha$ -Sn where the magnitude of the band gap energy ranges from 2.8 to 0.08 ev. These investigators considered that since there is no appreciable variation of the lattice constants for the compounds of each of these series, only the degree of ionic and covalent character can influence the magnitude of their band gaps. Thus, they considered that, in general, covalent bonding decreases the band gap energy of ionic crystals while the admixture of ionic bonding increases the gap energy of covalent crystals. Goodman (109) also suggests that an increase in ionicity will increase the width of the band gap. However, it should be noted that bond strengths of compounds as calculated by Manca (108), within each of the two isoelectronic series discussed above, can differ considerably from each other. The magnitude of these differences appear to be sufficiently great so that an entirely different interpretation can be realized. The above considerations indicate no more than strong trends since the range of basic parameters such as crystal structure, atomic radii, and electronic configuration is too wide for any simple rule to hold accurately.

From an empirical calculation of the single bond energy of binary semiconductors with a zincblende, wurtzite or diamond structure, Manca (108) plotted the bond energy as a function of the band gap energy and found that a linear correlation exists for most of these compounds. In Figure 7, plots similar to those of Manca were made using values for the band gap energies as given in Table 4. Equations for these lines were obtained and were found to be quite similar to those of Manca's. The lines shown in Figure 7 are given by

$$\text{IVB-IVB, } E_g = 2.13 (E_s - 1.35)\text{ev.} \quad (38)$$

$$\text{IIIB-VB, } E_g = 1.84 (E_s - 1.36)\text{ev.} \quad (39)$$

$$\text{IIB-VIB, } E_g = 1.68 (E_s - 2.14)\text{ev.} \quad (40)$$

where  $E_g$  is the band gap energy and  $E_s$  is the single bond energy.  $E_s$  was calculated according to Pauling's principle (42). Manca attributed the range in slopes 2.13 to 1.68 partly to the increasing ionic character of the bond, and in part to the effect of polarization of the component atoms. Because of the strong percentage of ionic bonding in GaN, AlN, and InN, values for these compounds lie on the group IIB-VIB line rather than on the group IIIB-VB line as would be expected. Manca also attributes to high ionicity the lack of correlation for the IB-VIIB compounds of zincblende structure and for materials such as ZnO and CdO, both of which possess a wurtzite structure. Contrary to the conclusions drawn by other investigators, Manca considers that within any grouping such as IIIB-VB semiconductors, the width of the band gap is greatest in the purely covalent semiconductors and diminishes with increasing ionic character of the bond. He attributes this to the fact that the state of localization of the electrons in molecular orbitals is greatest in the highly covalent semiconductors.

Sklar and co-workers (110, 111) have considered possible semiconductors which may result from a combination of group IIIA, rare-earth elements, with those of group VB. They decided that a really adequate theoretical treatment was quite difficult because of the "complexities of the coupling forces" but that an empirical expression for estimating the band gap energy could be obtained by comparison with IIIB-VB compounds, which are known to be semiconductors possessing a mixture of covalent and ionic bonding. This expression is shown as

$$E_g = \frac{1}{a} \log \left[ \frac{1}{(R_{\text{ion}}^{\text{III}})(R_{\text{cov}}^{\text{V}})} \right] \quad (41)$$

where  $\frac{1}{a}$  is a constant (approximately equal to 10 if  $E_g$  is in ev.), and  $R_{\text{ion}}^{\text{III}}$  and  $R_{\text{cov}}^{\text{V}}$  are the ionic and covalent radii (Å) of groups IIIB and VB respectively. By using this equation for some rare earth type compounds, it was concluded that rare earth phosphides and nitrides, if semiconductors, have a band gap energy in the range 1-3 ev.

Another class of rare earth compounds investigated by Sklar (110, 111) are the hexaborides. Preliminary optical measurements, made on selected rare earth nitrides and hexaborides in thin film form, yielded values which were interpreted as the optical transmission edge characteristic of semiconductors. The band gap

energy values, estimated from the wavelength of this edge, are shown in Table 4. Samsonov and Paderno are reported (112) to have carried out measurements of the resistivity and the Seebeck coef. of the hexaborides of La, Ce, Pr, Nd, Sm, and Gd and to have concluded that all hexaborides are p-type semiconductors.

In this section, many of the factors that can effect the work function of semiconductors were discussed. The external work function has been only slightly studied. The band gaps of semiconductors, which are related to the internal work function, have been determined for many such materials. However, correlations based upon crystalline structure and electronic configurations of the component elements are still in the qualitative stages. Accurate prediction of band gap energies requires consideration of a multitude of structural factors which has not yet been accomplished.

## 9. Summary

This report has been concerned with a fundamental study of emitter and collector materials in thermionic energy converters and the particular properties which tend to effect the theoretical efficiency of these converters. Since the efficiency of most types of thermionic converters is known to increase with high temperature operation, a search was initially made for all useful thermionic and high temperature data pertaining to refractory type materials having sufficiently low vapor pressures at the operating emitter and collector temperatures. The most important material variable was considered to be the work function and, consequently, a study of those factors, which if known would permit prediction of work function values, was undertaken. Basic physical and chemical properties of metals, semiconductors, and insulators that were considered to be important in this study concerning work functions were electron affinity, electronegativity, surface properties, strength and type of chemical bonding, etc. Quantitative theories concerning thermionic constants of refractory materials are limited. Such analyses have been attempted for the work function of group IA metals and also for ionic compounds such as the alkali halides and alkaline earth oxides. However, in these cases, agreement with experimental values was not completely satisfactory.

Specific solid compounds which are of interest as possible high temperature emitters include transition metalloids (diborides, carbides, and nitrides) and rare earth hexaborides. However, these materials have been investigated only on a purely qualitative basis, largely by Samsonov and his co-workers in Russia. In attempting to analyze and correlate for many such materials a number of different electrical properties, including the thermionic work function, Samsonov considered the importance of a gradual filling up of d shells in a transition metal and of the f shells in a rare earth metal. This was considered to be indicative of the extent of the screening of the outer electrons from the nuclear charge and involved the narrowing or widening of conduction bands which are created during compound formation.

Values for the apparent or effective work functions and Richardson A of most binary compounds which have appeared in the literature were compiled. The experimental data were usually obtained from solids that contained some impurities or defects in the crystalline lattice and which may frequently have possessed a contaminated surface. It was generally concluded that since the attempts to calculate work functions from basic principles are quite difficult, it is necessary to use qualitative methods for the production of relative values of work functions of interest. For this reason a qualitative analysis was initially made on the internal work function of semiconductors where an important parameter, the band gap energy, is known for many of these. Conflicting explanations have been expounded by different investigators in reference to this subject.

It is expected that most of the studies described in this summary report will be continued during 1962 with the emphasis between placed upon pure compounds and upon the influence thereon, of adsorbed monolayers on the surface, impurities in the lattice, bonding type, strength of bond, and radiation damage. At the same time, a theoretical study will be undertaken with regard to the electron affinity of solids and will include a study of such parameters as surface dipole layers, lattice spacing and orientation.

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TABLE I  
WORK FUNCTIONS OF THE ALKALI METALS

METAL	$r_s$	I + H	$E_f$	$\phi$ calc.	$\phi$ exp.
Li	3.28	7.04	2.07	2.19	2.28
Na	4.00	6.25	1.89	2.15	2.28
K	4.97	5.27	1.22	2.20	2.24
Rb	5.32	5.03	1.07	2.20	2.19
Cs	5.73	4.70	.92	2.15	1.87

TABLE 2

Values of Some Crystalline Parameters for Alkaline Earth Oxides

Compound	Lattice Spacing, Å	Lattice Energy, ev.	Vapor Pressure atm. (2000°K)	Metal Ionization Potential, ev.	Calculated Maximum Work Function, ev.	* Experimental Work Function, ev.
BaO	5.52	32.5	$1.0 \times 10^{-6}$	10.0	2.6	1.4 - 1.7
SrO	5.14	34.4	$6.9 \times 10^{-7}$	11.0	3.3	2.1 - 2.2
CaO	4.80	36.6	$2.1 \times 10^{-7}$	11.8	4.8	1.7 - 2.5
MgO	4.20	40.9	$5.0 \times 10^{-6}$	15.0	5.9	2.3 - 4.4
BeO	3.28	49**	$6.6 \times 10^{-9}$	18.1	11.2	3.8 - 4.7

\* See Table 3 for details and references

\*\* Estimated

TABLE 3  
Thermionic Emission Constants for Simple Chemical Compounds

Compound	Work Function, ev.	Rich A, Amps/cm <sup>2</sup> deg <sup>2</sup>	Ref.	Remarks*
<u>Oxides</u>				
C <sub>2</sub> O	0.75	0.1	14	φ <sub>A</sub>
	0.89-1.17	---	53	φ <sub>E</sub> , T = 400°K
BeO	3.8	---	54	φ <sub>E</sub> , T = 1400°K
	4.7	---	53	φ <sub>E</sub> , T = 1400°K
MgO	3.1	---	54	φ <sub>E</sub> , T = 1400°K
	4.4	---	53	φ <sub>E</sub> , T = 1400°K
	2.31-3.70	---	55	φ <sub>A</sub> , { Seven types of samples
	2.80-3.85	---	55	φ <sub>E</sub> , T = 1000°K } ranging from powder to
	2.50	---	16	φ <sub>E</sub> , T = 1000°K } sing crystal.
CaO	1.69	3 x 10 <sup>-4</sup>	57	φ <sub>A</sub>
	2.12	---	53	φ <sub>E</sub> , T = 1050°K
SrO	2.20	100	14	φ <sub>A</sub>
	1.5	.1	58	φ <sub>A</sub>
BaO	1.4	6	14	φ <sub>A</sub>
	1.66	---	53	φ <sub>E</sub> , T = 1050°K
Al <sub>2</sub> O <sub>3</sub>	4.4	---	54	φ <sub>E</sub> , T = 1400°K
B <sub>2</sub> O <sub>3</sub>	4.7	---	54	φ <sub>E</sub> , T = 1400°K
Sc <sub>2</sub> O <sub>3</sub>	3.8	---	54	φ <sub>E</sub> , T = 1400°K
	4.23	400	59	φ <sub>A</sub> , T = 1300-1700°K
	4.04	---	59	φ <sub>E</sub> , T = 1700°K

\* φ<sub>A</sub> = Apparent work function, φ<sub>E</sub> = Effective work function.

TABLE 3, cont.

Compound	Work Function, ev.	Rich A, Amps/cm <sup>2</sup> deg <sup>2</sup>	Ref.	Remarks
<u>Oxides, cont.</u>				
Y <sub>2</sub> O <sub>3</sub>	3.66	9.3	59	φ <sub>A</sub> , >1700°K
	3.16	---	14	φ <sub>E</sub> , T = 1900°K
	4.14	1000	59	φ <sub>A</sub> , T = 1300-1600°K
	3.87	---	59	φ <sub>E</sub> , T = 1600°K
	3.22	1.1	59	φ <sub>A</sub> , T >1600°K
	2.0	.55	60	φ <sub>A</sub>
La <sub>2</sub> O <sub>3</sub>	3.25	---	14	φ <sub>E</sub> , T = 1900°K
	2.50	.9	14	φ <sub>A</sub>
	2.80	---	60	φ <sub>A</sub>
	3.70	6.6	59	φ <sub>A</sub> , T = 1300-1800°K
	4.20	---	59	φ <sub>E</sub> , T = 1800°K
	2.95	0.004	59	φ <sub>A</sub> , T >1800°K
	3.18	31	61	φ <sub>A</sub>
	2.75	---	14	φ <sub>E</sub> , T = 1800°K
	2.3	1.0	14	φ <sub>A</sub>
	2.7	0.005-10	62	φ <sub>A</sub> + 20%. Rich A depends upon activation state of cathode.
Pr <sub>2</sub> O <sub>3</sub>	2.8	0.22	60	φ <sub>A</sub>
	1.9	0.1	64	φ <sub>A</sub>
	3.1	---	64	φ <sub>E</sub> , T = 1850°K
Nd <sub>2</sub> O <sub>3</sub>	2.0	0.2	64	φ <sub>A</sub>
	3.0	---	64	φ <sub>E</sub> , T = 1850°K
	2.3	0.99	60	φ <sub>A</sub>
	2.96	53	61	φ <sub>A</sub>
Sm <sub>2</sub> O <sub>3</sub>	3.32	285	63	φ <sub>A</sub> • Pulsed emission measurements
	2.38	2.0	64	φ <sub>A</sub>
	2.8	0.33	60	φ <sub>A</sub>

TABLE 3, cont.

Compound	Work Function, ev.	Rich A, Amps/cm <sup>2</sup> -deg. <sup>2</sup>	Ref.	Remarks
Eu <sub>2</sub> O <sub>3</sub>	3.1	---	64	φ <sub>E</sub> , T = 1850°K
	2.98	50	61	φ <sub>A</sub>
	2.48	0.3	64	φ <sub>A</sub>
	3.50	---	64	φ <sub>E</sub> , T = 1850°K
	2.6	0.11	60	φ <sub>A</sub>
Gd <sub>2</sub> O <sub>3</sub>	2.18	0.5	64	φ <sub>A</sub>
	3.1	---	64	φ <sub>E</sub> , T = 1850°K
	2.1	0.66	60	φ <sub>A</sub>
	2.58	24.2	63	φ <sub>A</sub>
	3.00	51	61	φ <sub>A</sub>
Tb <sub>2</sub> O <sub>3</sub>	2.1	0.22	60	φ <sub>A</sub>
	2.28	1.6	64	φ <sub>A</sub>
	3.0	---	64	φ <sub>E</sub> , T = 1850°K
	2.1	0.96	60	φ <sub>A</sub>
	2.3	0.33	60	φ <sub>A</sub>
Er <sub>2</sub> O <sub>3</sub>	2.4	0.76	60	φ <sub>A</sub>
	2.75	4	64	φ <sub>A</sub>
	3.3	---	64	φ <sub>E</sub> , T = 1850°K
	2.7	1.42	60	φ <sub>A</sub>
	2.3	0.11	60	φ <sub>A</sub>
Yb <sub>2</sub> O <sub>3</sub>	2.57	7.9	65	φ <sub>A</sub>
	2.55	3.3	66	φ <sub>A</sub>
	2.67	5.6	67	φ <sub>A</sub>
Lu <sub>2</sub> O <sub>3</sub>				
ThO <sub>2</sub>				

TABLE 3, cont.

Compound	Work Function ev.	Rich $A_2$ Amps/cm <sup>2</sup> deg <sup>2</sup>	Ref.	Remarks
	2.71	21	59	$\phi_A$ , T=1100-1300°K
	3.06	--	59	$\phi_E$ , T=1300°K
	1.66	0.001	59	$\phi_A$ , T>1300°K
	3.1	--	14	$\phi_E$ , T=1900°K
UO <sub>2</sub>	3.1	--	68	$\phi_A$
TiO <sub>2</sub>	4.7	--	54	$\phi_E$ , T=2000°K
	3.7	--	16	$\phi_E$ , T=2000°K
	3.87	0.458	59	$\phi_A$ , T=1500-2000°K
	4.2	--	54	$\phi_E$ , T=2000°K
ZrO <sub>2</sub>	3.9	--	14	$\phi_E$ , T=2000°K
	4.11	281	59	$\phi_A$ , T=1400-1700°K
	3.96	--	59	$\phi_E$ , T=1700°K
	3.12	0.363	59	$\phi_A$ , T>1700°K
HfO <sub>2</sub>	2.0	0.02	64	$\phi_A$
	3.6	--	64	$\phi_E$ , T=1900°K
	3.76	381	59	$\phi_A$ , T=1300-1500°K
	3.60	--	59	$\phi_E$ , T=1500°K
	2.82	0.49	59	$\phi_A$ , T>1500°K
SiO <sub>2</sub>	5.0	--	54	$\phi_E$ , T=2000°K

TABLE 3 cont.

Compound	Work Function, ev.	Rich A Amps/cm <sup>2</sup> deg <sup>2</sup>	Ref.	Remarks
<u>Borides</u>				
TiB <sub>2</sub>	3.95	--	69	φ <sub>E</sub> ' (?)
	4.6	670	70	φ <sub>A</sub> ' Poisoning from evaporation of tungsten heater.
VB <sub>2</sub>	3.88	--	69	φ <sub>E</sub> ' (?)
	4.2	.1	70	φ <sub>A</sub> ' Poisoning from evaporation of tungsten heater.
CrB <sub>2</sub>	3.36	--	69	φ <sub>E</sub> ' (?)
	4.1	19	70	φ <sub>A</sub> ' Poisoning from evaporation of tungsten heater
MnB <sub>2</sub>	4.14	--	69	φ <sub>E</sub> ' (?)
	3.70	--	69	φ <sub>E</sub> ' (?)
ZrB <sub>2</sub>	4.2	317	70	φ <sub>A</sub> ' Poisoning from evaporation of tungsten heater
	4.48	3x10 <sup>4</sup>	66	φ <sub>A</sub> ' Stoichiometry not certain
NbB <sub>2</sub>	3.65	--	69	φ <sub>E</sub> ' (?)
	4.0-4.3	1.7-10.7	70	φ <sub>A</sub> ' Poisoning from evaporation of tungsten heater
MoB <sub>2</sub>	3.38	--	69	φ <sub>E</sub> ' (?) Stoichiometry may be Mo <sub>2</sub> B <sub>5</sub>
	2.9	3x10 <sup>-9</sup>	70	φ <sub>A</sub> ' MoB <sub>2</sub> apparently does not exist at room temp, but may exist at high temperatures.

TABLE 3 Cont.

Compound	Work Function, ev.	Rich A Amps/cm <sup>2</sup> deg <sup>2</sup>	Ref.	Remarks
TaB <sub>2</sub>	3.5	.2	70	φ <sub>A</sub> , Poisoning from evaporation of tungsten heater.
TaB	2.89	10	66	φ <sub>A</sub> , Several percent TaB <sub>2</sub> probably present
W <sub>2</sub> B <sub>5</sub>	2.62	--	69	φ <sub>E</sub> , (?) Reference lists compound as WB <sub>2</sub> , which probably does not exist except perhaps near melting point (92).
UB <sub>2</sub>	3.3	--	68	φ <sub>A</sub>
CaB <sub>6</sub>	2.86	2.6	71	φ <sub>A</sub>
SrB <sub>6</sub>	2.67	0.14	71	φ <sub>A</sub>
BaB <sub>6</sub>	3.45	16	71	φ <sub>A</sub>
ScB <sub>6</sub>	2.96	4.6	72	φ <sub>A</sub>
YB <sub>6</sub>	2.20	15	73, 74	φ <sub>A</sub>
LaB <sub>6</sub>	2.66	29	71	φ <sub>A</sub>
CeB <sub>6</sub>	2.68	73	74	φ <sub>A</sub>
CeB <sub>6</sub>	2.59	3.6	71	φ <sub>A</sub>
PrB <sub>6</sub>	3.46	300	74	φ <sub>A</sub>
NdB <sub>6</sub>	3.97	420	74	φ <sub>A</sub>

TABLE 3, cont.

Compound	Work Function, ev.	Rich A Amps/cm <sup>2</sup> deg <sup>2</sup>	Ref.	Remarks
SmB <sub>6</sub>	4.4	---	75	$\phi_{A_1} (?)$
EuB <sub>6</sub>	4.9	$1 - 5 \times 10^3$	75	$\phi_A$
GdB <sub>6</sub>	2.05	0.81	74	$\phi_A$
	4.0 - 4.2	6.6 - 1590	70	$\phi_A$ , Poisoning from evaporation of tungsten heater
TbB <sub>6</sub>	6.0	---	76	$\phi_A$
DyB <sub>6</sub>	3.53	25.1	74	$\phi_A$
HoB <sub>6</sub>	3.42	13.9	74	$\phi_A$
ErB <sub>6</sub>	3.37	9.9	74	$\phi_A$
YbB <sub>6</sub>	3.13	2.5	74	$\phi_A$
LuB <sub>6</sub>	3.0	0.36	74	$\phi_A$
ThB <sub>6</sub>	2.92	0.5	71	$\phi_A$
LaB <sub>12</sub>	2.16	---	77	$\phi_{E_1} (?)$
CeB <sub>12</sub>	2.20 - 2.24	---	77	$\phi_{E_1} (?)$
<u>Nitrides</u>				
TiN	3.96	---	66	$\phi_{E_1}$ T = 2000°K, Poisoning from excessive evaporation of emitter

TABLE 3, cont.

Compound	Work Function, ev.	Rich A Amps/cm <sup>2</sup> deg <sup>2</sup>	Ref.	Remarks
ZrN	3.96	---	66	$\phi_E$ , T = 2000°K, Poisoning from excessive evaporation of emitter
BN	4.0	---	66	$\phi_E$ , T = 2000°K Poisoning from excessive evaporation of emitter
UN	3.1	---	68	$\phi_A$
<u>Carbides</u>				
ThC <sub>2</sub>	3.5	550	66	$\phi_A$
	3.2	100	14	$\phi_A$ , Exact sample stoichiometry not known
UC	3.62	90	78, 79	$\phi_A$ , Fused UC, T <1590°K
	2.67	3.5	78, 79	$\phi_A$ , Fused UC, T >1610°K
	4.57	7.2 x 10 <sup>5</sup>	78	From Log J <sub>e sat</sub> vs T plot.
	2.94	33	80	$\phi_A$ , Powdered UC
ZrC <sub>0.8</sub> UC <sub>0.2</sub>	4.3	6.6 x 10 <sup>4</sup>	78	From log J <sub>e sat</sub> vs T plot.
	3.1	12	81	$\phi_A$ , Hot pressed sample.
	3.53	55 $\alpha$	79	$\phi_A$ , Fused sample, T <1610°K
	2.53	0.3	79	$\phi_A$ , Fused sample, T >1650°K
TiC	3.35	25	66	$\phi_A$
HfC	4.0	40	113	$\phi_A$

TABLE 3, cont.

Compounds	Work Function, ev.	Rich A <sub>2</sub> , Amps/cm <sup>2</sup> deg. <sup>2</sup>	Ref.	Remarks
ZrC	2.18	0.31	66	φA, Powdered ZrC
	2.3	0.2	14	φA, Powdered ZrC
	3.8	134	78	φA, Fused ZrC
	4.0	140	81	φA, Fused ZrC
	3.5	64	14	φA
	3.14	.3	66	φA
<u>Sulfides</u>				
CaS	2.1	.06-4400	83	φA, Rich A depends upon activation of cathode and method of preparation.
	2.38	---	83	φE, T = 1113-1313°K
	2.54	---	83	φE, T = 1113-1313°K
	2.61	---	82	φE, T = 1113-1313°K
<u>Selenides</u>				
CaSe	2.70	---	83	φE, T = 1043-1373°K
	2.57	---	83	φE, T = 1043-1373°K
	2.07	---	83	φE, T = 1043-1373°K

TABLE 4  
APPROXIMATE BAND GAPS (ev) IN SOME SIMPLE SOLIDS

<u>IIIB</u>	<u>IB - VIIB</u>	<u>IIIB - VB</u>	<u>IIIB - VIB</u>
B	1.0-1.5	CrBr (5)	AIP 3.0
<u>IVB</u>		AgBr 2.9	GaP 2.25
		CuI 2.8	InP 1.27
		AgI 2.8	BAAs (3.0)
C	(3.0)	AlAs 2.16	AlAs 2.16
C(dia)	5.42	GaAs 1.4	GaAs 1.4
Si	1.1	InAs 0.36	InAs 0.36
Ge	0.66	BSb *2.6	BSb *2.6
$\alpha$ -Sn	0.08	AlSb 1.65	AlSb 1.65
Pb	metal	GaSb 0.81	GaSb 0.81
*CeSn	0.40	InSb 0.16	InSb 0.16
$\alpha$ -SiC	3.12		
$\beta$ -SiC	2.2		
SiGe	0.92		
*SiSn	0.59		
<u>VB</u>			
P(yel)	2.1	<u>IB - VIB</u>	<u>IB - VIB</u>
(red)	1.5	Cu <sub>2</sub> O (1.2)	In <sub>2</sub> S <sub>3</sub> 2.3
As(grey)	1.2	Cu <sub>2</sub> Te 0.95	Al <sub>2</sub> Se <sub>3</sub> 3.1
$\beta$ -Sb	0.11	Ag <sub>2</sub> Te 0.95	Ga <sub>2</sub> Se <sub>3</sub> 1.9
		Ag <sub>2</sub> S 0.90	In <sub>2</sub> Se <sub>3</sub> 1.25
<u>VIB</u>		<u>IIIB - VB</u>	Ga <sub>2</sub> Te <sub>3</sub> 1.2
		BN (5.0)	In <sub>2</sub> Te <sub>3</sub> 1.0
$\alpha$ -S	2.6	AlN 3.8	GaS 2.6
Se	1.8	GaN 3.25	GaSe 2.0
Te	0.37	InN *2.5	InSe 1.8
		BP *4.2-5.9	TiSe 0.57
			GaTe 1.7

\*Values are estimated by Manca (108).

Values in parenthesis are uncertain.

TABLE 4 cont.

IVB - VIB	IA - VIIB	IIA - IVB	IIIA - IIIB
PbO 2.35	LiF (12)	Mg <sub>2</sub> Si 0.77	LaB <sub>6</sub> 1.9
GeS 1.8	NaF ↓	Mg <sub>2</sub> Ge 0.7	NdB <sub>6</sub> (4)
SnS 1.25	KF (9)	Mg <sub>2</sub> Sn 0.25	GdB <sub>6</sub> 3.2
PbS 0.38	CsF (10)	Mg <sub>2</sub> Pb Metal	DyB <sub>6</sub> (4)
SnSe (0.88)	LiCl ↓	Ca <sub>2</sub> Si 1.9	ErB <sub>6</sub> 3.6
PbSe 0.26	NaCl 8.5	Ca <sub>2</sub> Sn 0.9	IIIA - VB
PbTe 0.28	KCl 8.5	Ca <sub>2</sub> Pb 0.45	YN 1.9
VB - VIB	CsCl ↓	Ca <sub>3</sub> Pb <sub>2</sub> 2.2	DyN 2.1
As <sub>2</sub> O <sub>3</sub> (4.0)	LiBr 7.5	IIA - VB	HoN 1.9
Sb <sub>2</sub> O <sub>3</sub> 4.2	NaBr (7)	Mg <sub>3</sub> Sb <sub>2</sub> 0.8	ErN 3.0
α-Bi <sub>2</sub> O <sub>3</sub> 3.2	KBr	Mg <sub>3</sub> Bi <sub>2</sub> Metal	MISCELLANEOUS
As <sub>2</sub> S <sub>3</sub> 2.5	RbBr	IIA - VIB	TiO <sub>2</sub> 3.0
Sb <sub>2</sub> S <sub>3</sub> 1.7	CsBr	BeO (7)	NiO 2.4
Bi <sub>2</sub> S <sub>3</sub> 1.3	LiI	MgO 7.3	MoS <sub>2</sub> 0.6
As <sub>2</sub> Se <sub>3</sub> 2.5	NaI	CaO 5.6	BiI <sub>3</sub> 1.1
Sb <sub>2</sub> Se <sub>3</sub> 1.25	KI	SrO 5.7	
Bi <sub>2</sub> Se <sub>3</sub> 0.35	RbI	BaO 5.1	
As <sub>2</sub> Te <sub>3</sub> (1)	CsI	SrS (4.1)	
Sb <sub>2</sub> Te <sub>3</sub> 0.3	IA - VB		
Bi <sub>2</sub> Te <sub>3</sub> 0.15	Na <sub>3</sub> Sb 1.1		
BiSe 0.4	K <sub>3</sub> Sb 0.8-1.1		
	Rb <sub>3</sub> Sb 1.0		
	Cs <sub>3</sub> Sb 0.6-1.6		
	Cs <sub>3</sub> Bi (0.55)		
	K <sub>3</sub> Sb (0.9)		
	CsBi <sub>2</sub> 1.65		

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