Studies on Cathode-Materials. Part 1.
On the Zone-Model of the Oxide-Cathodes.

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1. Introduction. The thermionic emission and other behaviours of oxide cathodes have been extensively investigated theoretically as well as technically by many authors. However, a complete picture of the thermionic emission of the oxide cathodes which can explain the many experimental results, has not been given, since the phenomena of the thermionic emission of the oxide cathodes are very complicated.

It appears that metallic atoms are formed in the oxide crystals by the decomposition of the oxides and the system consists of the "impurity semiconductor" whose model has been given by Wilson.(1) Therefore, it may be a reasonable picture that the thermionic emission of the oxide cathodes occurs in the composite system, consisting of the semiconductor and the metallic atoms which are formed on the surface of the semiconductor.

We wish to propose a zone model, based on the quantum mechanical theory of solid state, which can completely explain the mechanism of the thermionic emission and other properties of the oxide cathodes.

2. Résumé of the experimental results. Of the oxide cathodes, especially the alkaline earth metal oxides have been extensively investigated, since they are technically of great importance, but some of the experimental results on the properties of the oxides observed by several authors have not always coincided with each other. The important experimental results which have been supported by most of the authors, are described as follows.

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(1) H. A. Wilson: *Proc. Roy. Soc.*, (London), A, **133** (1931), 458; **134** (1932), 277; **136** (1932), 487.

(a) It is believed that the oxide cathodes can emit enough electrons only after the operation of activation, but the oxide itself can scarcely emit electrons. Metallic atoms are formed on the surface of the oxides, and they are responsible for the thermionic emission.(2) ~ (12)

(b) The thermionic emission current varies with the amount of the metallic atoms adsorbed on the surface of the oxides, as in the case of the alkaline metals or alkaline earth metals on the tungsten or other metal filaments. It is believed that the optimum activity is obtained, when the oxide surface is covered with a single layer of the adsorbed metallic atoms, i.e. the fraction of the surface (θ) covered with metallic atoms is equal to unity.(2),(3)

(c) The dependence of the thermionic current of the oxide cathodes on the temperature is given by the so called Richardson's equation,(13) ~ (16) as in the case of pure metals, that is

$$i_s = AT^2 e^{-b_0/kT} \qquad (1),$$

with $k =$ Boltzmann constant,

$i_s =$ saturation thermionic current,

$A =$ constant,

$b_0 =$ thermionic work function,

$T =$ absolute temperature.

(d) By the Huxford's experiment,(17) the photoelectric work function of alkaline earth metal oxide cathodes is equal to the thermionic work function. This experimental result is of great importance, since it can give a direct method to decide the model of the oxide cathodes, as we shall discuss in detail in the following sections.

3. Theory. A. *Energy levels in the oxide crystals.* Alkaline earth oxide crystals are insulators since p-band of O^{--} ions directly below the conduction band lies in the range of, at least, 10 eV from the conduction band and, therefore, we can practically neglect the number of the electrons

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(2) L. R. Koller: *Phys. Rev.*, **22** (1925), 671.
(3) J. A. Becker: *Phys. Rev.*, **34** (1929), 1323; **38** (1931), 2193.
(4) H. Rothe: *Z. f. Physik*, **36** (1926), 737.
(5) W. Espe: *Wiss. Veröff. a. d. Siemens Konz.*, **5** (1927), 5, 46.
(6) F. Detels: *Jahrb. d. drahtl. T.*, **30** (1927), 30, 52.
(7) M. S. Glass: *Phys. Rev.*, **28** (1926), 521.
(8) E. F. Lowry: *Phys. Rev.*, **35** (1930), 1367.
(9) A. Gehrts: *Z. tech. Phys.*, **11** (1930), 246; *Naturwiss.*, **20** (1932), 732.
(10) A. L. Reiman, R. Murgoci: *Phil. Mag.*, **8** (1930), 440.
(11) S. Dushman: *Rev. Mod. Phys.*, **2** (1930), 493.
(12) De Boer: Elektronenemission und Adsorptionserscheinungen, Leipzig, (1937).
(13) A. Sommerfeld: *Z. Physik.*, **47** (1920), 1.
(14) R. H. Fowler: *Proc. Roy, Soc.*, (London), A, **117** (1928), 549; **122** (1929), 36.
(15) L. Nordheim: *Phys. Z.*, **30** (1929), 177.
(16) W. Howston: *Z. Physik*, **47** (1928), 33.
(17) W. S. Huxford: *Phys. Rev.*, **38** (1931), 379.

which can enter into the conduction band from p-band of O^{--} ions by the Fermi distribution.

It is well known that metallic atoms diffuse into the crystal, after the oxides were heated in the vacuum(18) or the filament covered with the oxides was heated by the electric current. We know that such oxides may be represented by the semiconductor model which was proposed by Wilson.(1),(19)

Fig. 1 shows the energy levels in the oxide crystals which are obtained by the same method described previously by one(20) of the authors in the study of the zinc sulphide crystal-phosphors.

In this figure, M is the alkaline earth metal atom level (which we wish to call impurity atom level), O^{--} is divalent negative oxygen ion, M^{+} and M^{++} are respectively monovalent and divalent positive ions of alkaline earth metal.

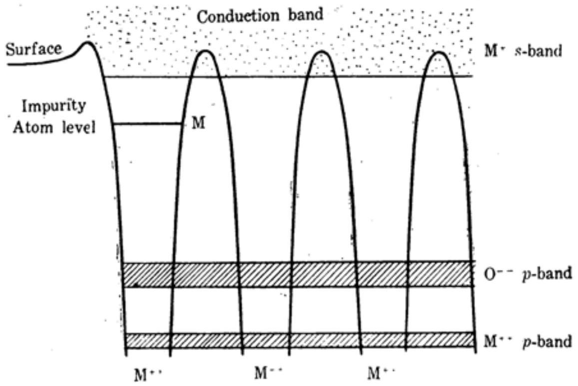

Fig. 1.

In CaO, the energy gap between conduction band and p-band of O^{--} ions is about 23 eV. Also in SrO and BaO, energy band of O^{--}, Sr^{++} or Ba^{++} ions lie about in the same range as CaO.

Energy level of impurity atom, i.e. Ca, Sr, or Ba, lies in the range from about 2 eV to 4 eV below the conduction band in the individual oxide crystal and the energy gap may be smaller in the order of BaO, SrO and CaO.

B. *Mechanism of the thermionic emission of oxide cathodes.* Let us consider the mechanism of the thermionic emission of oxide cathodes by using the semiconductor model obtained above.

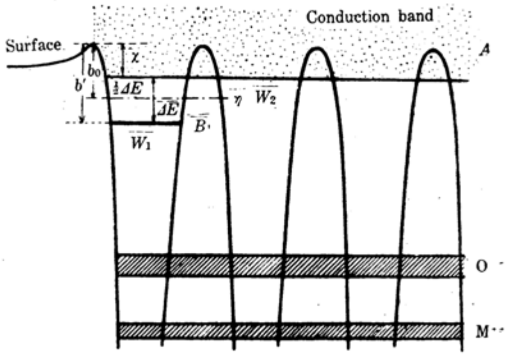

Fig. 2.

In Fig. 2, A is the conduction band and B is the energy level of the impurity atom.

Suppose that the energy gap between A and B is equal to ΔE, then thermodynamical function η is given by(21)

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(18) H. Schriel: *Z. anorg. Chem.*, **231** (1937), 313.
(19) R. H. Fowler, A. H. Wilson: *Proc. Roy. Soc.*, (London), A, **137** (1932), 503.
(20) Y. Uehara: *J. Chem. Soc. Japan*, **60** (1939), 133.
(21) H. Frölich: "Elektronentheorie der Metalle," Berlin, (1936), 226.

$$\eta = \frac{W_2 - W_1}{2} + \frac{kT}{2} \log \left(\frac{|m_1| kT}{2\pi \left(\frac{h}{2\pi} \right)^2 n_a{}^{2/3}} \right)^{3/2} \qquad (2),$$

with

n_a = number of electrons in the B-level per unit volume,

h = Planck's constant,

m_1 = effective mass of the electrons in the B-level,

W_1 = potential energy of the B-level,

W_2 = mean potential energy of the conduction band.

We can obtain the thermionic current emitted from the impurity level by using the same method of calculation for the electric conductivity of semiconductor by Wilson.(22)

Let the velocity of the electrons in the conduction band be $(u,v,w,)$ and u the velocity component perpendicular to the potential barrier at the surface, then the distribution function of the electrons in the conduction band is given by(21),(22)

$$n_2(u,\ v,\ w) = 2\left(\frac{m}{h}\right)^3 \cdot B \cdot (kT)^{-3/4} \cdot \exp\left\{ -\frac{1}{2}(W_2 - W_1) - \frac{1}{2} m (u^2 + v^2 + w^2) \right\} \Big/ kT \qquad (3),$$

with

$$B = \frac{n_a{}^{1/2}}{2^{5/4}} \left(\frac{h^2}{\pi m} \right)^{3/4} \qquad (4).$$

Suppose that the transmission coefficient of the potential barrier at the surface is $D(E)$. Then the thermionic current through the unit area on the surface per unit time is given by

$$i_s = \frac{4\pi m \varepsilon}{h^3} \cdot B \cdot (kT)^{1/4} \cdot e^{-\frac{1}{2}\Delta E/kT} \int_0^\infty D(E) \cdot e^{-U/kT} dU \qquad (5).$$

with

$$U = \frac{1}{2} m u^2 , \qquad E = U + \frac{1}{2} m (v^2 + w^2) ,$$

ε = electronic charge.

As the simplest case we put the boundary conditions as follows:

$$\begin{aligned} D(E) &= 1 , \text{ if } E \geq W_2 + \chi \\ &= 0 , \text{ if } E < W_2 + \chi \end{aligned} \qquad (6),$$

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(22) H. Wilson: *Proc. Roy. Soc.*, (London), A, **136** (1932), 487.

we can integrate easily above equation

$$i_s = \varepsilon n_a{}^{1/2} \cdot \left\{ \frac{2^3 m \pi k^5}{h^6} \right\}^{1/4} \cdot T^{5/4} \cdot e^{-\left(\frac{1}{2}\Delta E + \chi\right)/kT} \tag{7.}$$

If we compare eq. (7) with eq. (1), we can see that, apart from the constant term, eq. (7) involves term $T^{5/4}$ instead of term T^2 in eq. (1). Since we can not distinguish $T^{5/4}$ and T^2 experimentally, eq. (7) coincides with Richardson's equation formally and the thermionic work function is given by

$$b_0 = \frac{1}{2}\varDelta E + \chi \tag{8.}$$

The electrical conductivity of the semiconductor is approximately given by

$$\sigma = \sigma_0 e^{-\frac{1}{2}\Delta E/kT} \tag{9}$$

where σ_0 is a constant which is approximately independent of temperature. It is interesting that eq. (8) and eq. (9) involve the factor of $\frac{1}{2}\varDelta E$ instead of $\varDelta E$ as the activation energy.

In the model shown in Fig. 2, the photoelectric work function is given as follows, at least, under the conditions of (6),

$$b' = \varDelta E + \chi \tag{10}$$

As we mentioned in (d), the thermionic work function should be equal to the photoelectric work function. However, b_0 is not equal to b', if we compared eq. (9) with eq. (10). As the results, we can say that the thermionic emission of the oxides is not caused directly from the impurity atoms in the oxides.

In order to interpret correctly the behaviours of the oxide cathodes, we should take into account the metallic atoms adsorbed on the surface of the semiconductor.

As the ideal case, we consider first the case of $\theta = 1$. In the alkaline earth metals with two dimensional regular lattice, s-band of the valency electrons overlaps partially with the empty band directly above it, and the Fermi surface lies about in the middle of the overlapping part, as we see in Fig. 3.

The state which the surface of the semiconductor, shown in Fig. 2, is covered with the monoatomic layer of the metal, whose structure was mentioned above, is shown in Fig. 4.

Electrons in the metal layer and semiconductor exsist in the thermal equilibrium. Under this condition, the Fermi surface in the metal lies about in the middle of A and B, i.e.

$$\eta = \frac{1}{2}(W_2 - W_1) - kT \log \{B(kT)^{-3/4}\} ,$$

where the energy value of the second term is about 0.16 eV for the value of, for example, $n_a = 10^{18}$ and $T = 1000°\mathrm{K}$. Therefore we can neglect the second term, compared with the first term, which is about 1 eV, since we do not need the accurate value of η in the following discussion.

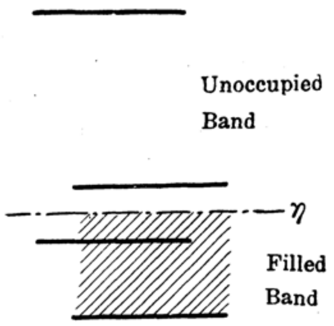

Fig. 3.

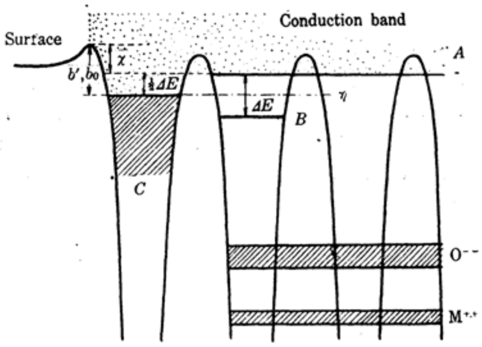

Fig. 4.

In the model shown in Fig. 4, electrons in the C-band are emitted over the potential barrier at the surface· after they have absorbed heat energy. The electrons emitted from the C-band are supplied by the electrons which have been thermally raised in the conduction band of the semiconductor from the impurity atoms.

Then the thermionic current is given by eq. (1) and the thermionic work function is given by

$$b_0 = \frac{1}{2}\Delta E + \chi \ .$$

If we recognize that the photoelectrons are emitted from C-band the photoelectric work function is given by

$$b' = \frac{1}{2}\Delta E + \chi \ .$$

As the results, the thermionic work function coincides with the photoelectric work function, as we have expected from the experimental result (d).

The behaviours of (a) and (b) in the adsorbed metal layer have been already discussed by many authors. De Boer proposed an atomic picture for the adsorbed atom layer. Therefore, we need not discuss about (a) and(b) in detail here, but only state that we must regard the metal layer as the two dimensional lattice, at least, locally even when θ is less than unity, although De Boer's atomic picture does not need such a condition.

Next we wish to consider the thermionic emission of the solid solution between BaO and SrO. In this solid solution, the lattice constant a becomes linearly larger as the SrO mol percentage increases.(23) Also, one of the authors has confirmed that maxima of the fluorescence bands of the zinc-cadmium sulphide crystalphosphors shift linearly from blue to red with increasing lattice constant. The lattice constant a increases

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(23) W. G. Burgers: *Z. Physik*, **80** (1933), 352.

linearly with increasing CdS mol percentage, as we shall report in the next paper.

If we apply zone theory of solid state,(24) to these experimental results, we can probably expect that the energy difference between conduction band and impurity level (or that between the excited state and ground state of the impurity atom) becomes linearly smaller with increasing SrO and CdS mol percentage in the individual solid solution.

As the results, the work function of the solid solution between BaO and SrO may become smaller as the SrO mol percentage is increased. And in this solid solution, we suppose that first the impurity level is caused from the Ba atom and later, in the case of large SrO mol percentage, it may be caused mainly from the Sr atom. Then we can expect that the thermionic emission current may become optimum when the SrO mol percentage takes a certain suitable amount. In fact, the optimum value of SrO is from about 50 to 60 percentage.

C. *Fluorescence of the alkaline earth oxides.* J. Ewles(25) reported that the alkaline earth oxides which contain no impurities as activator show fluorescence bands in the visible part, that is to say, in CaO at 6200Å and in BaO at 4650Å, 5629Å and 5970Å.

It may be proper to assume that these fluorescence bands are correlated with the alkaline earth metal level in the oxide crystals. As the probable picture, we wish to propose the following mechanism of fluorescence. That is to say, these fluorescence bands are responsible for the transitions of the electron from the excited states *nsnp* to the ground state ns^2 of the impurity atom, as we see in Fig. 5. Such a impurity atom level lies in the range from about 2 eV to 4 eV below the conduction band, as we have mentioned above. Studies of such a problem of fluorescence are very interesting and important in relation to the problem of the thermionic emission phenomena of the oxides.

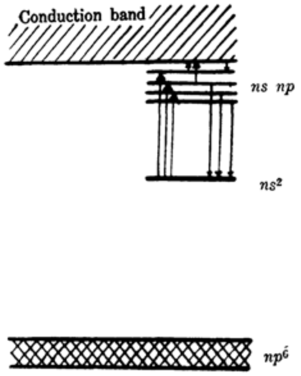

Fig. 5.

After we have written this paper, we received a paper of Blewett.(26) In his paper, he also obtained the same equation as eq. (7) in our paper, but as we have already discussed, eq. (7) does not coincide with the experimental results given in (d) of section 2.

In conclusion, we wish to express our sincere thanks to Vice-Director B. Imamura of this institute for his generous help, and also to Prof. S. Mizushima of Tokyo Imperial University for his kind advices and encouragement.

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(24) N. F. Mott, H. Jones: "The Theory of the Properties of Metals and Alloys," Oxford, (1936), 99.
(25) J. Ewles: *Proc. Roy. Soc.*, (London), **167** (1938), 34.
(26) J. P. Blewett: *J. App. Phys.*, **10** (1939), 668.