

## The Surface Photoelectric Effect

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Theoretical expressions describing the photoelectric emission from a metal surface are derived, taking account of the dependence, established by Bardeen, of the effective surface barrier on the momentum of the impinging electron, due to exchange and correlation forces in the interior. This generalization reduces by a significant factor the magnitude of the theoretical expression for the absolute photoelectric yield. The shapes of the energy and spectral distributions of emitted photo-electrons are essentially unchanged, so that certain well-known disagreements between theoretical and observed distributions near the threshold remain unexplained. The influence of the transmission coefficient of the surface potential barrier on the photoelectric properties of a metal is discussed and an experiment is proposed for determining directly the variation with energy of the transmission coefficient, thus leading to information concerning the shape of the barrier.

### I. INTRODUCTION

THE photoelectric current from a metal surface is influenced near the threshold, in its dependence on frequency and temperature, primarily by the factors describing the energy distribution of electrons in the metal and the transmission coefficient of the surface potential barrier. Existing theories dealing with the energy and spectral distributions of the emitted electrons make use of a free-electron model for the metal, with various assumptions concerning the surface barrier and the probability of excitation of the electrons. Rudberg<sup>1</sup> has examined and classified these assumptions.

The theory of the spectral and "normal" energy distributions, given by Fowler<sup>2</sup> and DuBridge<sup>3</sup> respectively, are based on the assumption of a barrier transmission coefficient which is constant for electrons with sufficient energy to escape, corresponding approximately to an image field barrier. While experimental results for a number of metal surfaces agree well<sup>4</sup> with these theories, results for sodium, which should approximate closely to the free-electron model, show marked systematic disagreements.<sup>5,6</sup> The work of Hill<sup>7</sup> on the total energy distribution for sodium shows that in this case also the image field theory is inadequate.

In an investigation of conditions at the surface of an ideal metal, Bardeen<sup>8</sup> has shown that, as a result of exchange and correlation forces in the electron gas the effective barrier for an electron depends in general on its momentum, and that the potential exhibits an asymptotic approach to an image field outside the surface. The exchange forces arise from the interaction in the motions of the electrons, due to the fact that electrons of parallel spin tend to keep apart, and Bardeen's

calculations show that the effective surface barrier is due primarily to these forces, while the ordinary electrostatic forces are of minor importance.

It has been pointed out recently by Makinson<sup>9</sup> that the momentum-dependence of the barrier has a marked effect on formal expressions for the photoelectric current and may well alter considerably the quantitative conclusions from earlier theories. It is one of the purposes of the present paper to determine the modifications necessary in the theoretical description of the photoelectric effect, when account is taken of this dependence. It is found that this generalization introduces a significant factor into the theoretical value of the photoelectric yield, reducing the latter for sodium by a factor of about 3 near the threshold. However, it does not materially alter the distribution functions of the photo-electrons, so that it is insufficient to resolve the disagreements with experiment mentioned above.

Attempts have been made to explain these discrepancies by assuming that the cleanest sodium surfaces obtainable in practice are far from "ideal" and that instead of being nearly constant, the barrier transmission coefficient varies greatly with the energy of the emitted electrons. Houston<sup>10</sup> obtained agreement with experimental results for the spectral and "normal" energy distributions by assuming that the transmission coefficient vanishes linearly with diminishing energy of the ejected electron, while Hill<sup>7</sup> postulated a coefficient with a selective maximum in order to explain the observed total energy distribution. In Sections IV and V below this aspect is reviewed and an experiment is proposed which should allow a direct determination of the transmission coefficient as a function of energy.

### II. THE EXCHANGE OPERATOR

It will be assumed<sup>8</sup> that the conduction electrons in the metal are subject to exchange interaction, but in the interior are otherwise free, moving in the "smeared" field of the combined positive and negative charges. The wave function then satisfies the unperturbed

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<sup>1</sup> E. Rudberg, *Phys. Rev.* **48**, 811 (1935).

<sup>2</sup> R. H. Fowler, *Phys. Rev.* **38**, 45 (1931).

<sup>3</sup> L. A. DuBridge, *Phys. Rev.* **43**, 727 (1933).

<sup>4</sup> See A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena* (McGraw-Hill Book Company Inc., New York, 1932).

<sup>5</sup> M. M. Mann and L. A. DuBridge, *Phys. Rev.* **51**, 120 (1937).

<sup>6</sup> C. F. Overhage, *Phys. Rev.* **52**, 1039 (1937).

<sup>7</sup> A. G. Hill, *Phys. Rev.* **53**, 184 (1938).

<sup>8</sup> J. Bardeen, *Phys. Rev.* **49**, 653 (1936).

<sup>9</sup> R. E. B. Makinson, *Phys. Rev.* **75**, 1908 (1949).

<sup>10</sup> W. V. Houston, *Phys. Rev.* **52**, 1047 (1937).

equation

$$-(\hbar^2/2m)\nabla^2u + V(\mathbf{r})u - \mathcal{G}(\mathbf{r})u = i\hbar\partial u/\partial t, \quad (1)$$

where  $V(\mathbf{r})$  is the Coulomb potential energy and  $\mathcal{G}(\mathbf{r})$  represents the exchange operator, defined by

$$\mathcal{G}(\mathbf{r})u_j(\mathbf{r}) = \frac{1}{2}e^2 \int \frac{\rho(\mathbf{r}, \mathbf{r}')u_j(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|},$$

in which  $\rho(\mathbf{r}, \mathbf{r}')$  is the Dirac density matrix,

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_i u_i^*(\mathbf{r})u_i(\mathbf{r}').$$

Dirac<sup>11</sup> has shown that if the exchange operator  $\mathcal{G}(\mathbf{r})$  acts on a plane-wave function  $\exp(i\mathbf{k}\cdot\mathbf{r})$  in the interior of a metal, where all states for which  $k = |\mathbf{k}| \leq k_0$  are filled, it has the effect of multiplying the wave function by a constant,  $A(k)$ , given by

$$A(k) = (e^2k_0/2\pi)f(k/k_0),$$

where the function  $f$  is defined by

$$f(x) = 2 + (1/x)(1-x^2) \ln\{(1+x)/|1-x|\}.$$

The corresponding results for electrons near the surface have been calculated by Bardeen.<sup>8</sup>

The energy of an electron in the state  $\mathbf{k}$  is then given by

$$E_k = (h/\mu)k^2 + V(-\infty) - A(k) = (h/\mu)k^2 - hv_k, \quad (2)$$

where  $\mu = 8\pi^2m/h$  and  $hv_k$  is the effective height of the surface potential barrier for this electron.

A good approximation to Dirac's theoretical expression<sup>12</sup> can be obtained near  $k = k_0$  by putting

$$A(k) = A_0 - \beta(h/\mu)k^2, \quad (3)$$

where  $A_0$  and  $\beta$  are constants. The dimensionless quantity  $\beta$  can be regarded as a measure of the magnitude of the exchange energy; when the latter is neglected,  $\beta = 0$ .

### III. THE PHOTOELECTRIC CURRENT

By regarding as a small perturbation the incident plane waves of light of frequency  $\nu$ , Makinson<sup>9</sup> has derived a formal expression, valid for any surface barrier, for the photoelectric current density from a simple metal. He showed that the contribution to the current, arising from electrons from the state  $\mathbf{k}$ , could be expressed in the form of the product of the electronic charge, the density of electrons in the state  $\mathbf{k}$ , the transmission coefficient of the surface barrier for the excited electrons, and an excitation function,  $X(\mathbf{k}, \nu)$ . Thus

$$dJ = -e4|\alpha_k|^2D(r)X(\mathbf{k}, \nu),$$

<sup>11</sup> P. A. M. Dirac, Proc. Camb. Phil. Soc. 26, 376 (1930).

<sup>12</sup> See reference 8, Fig. 1.

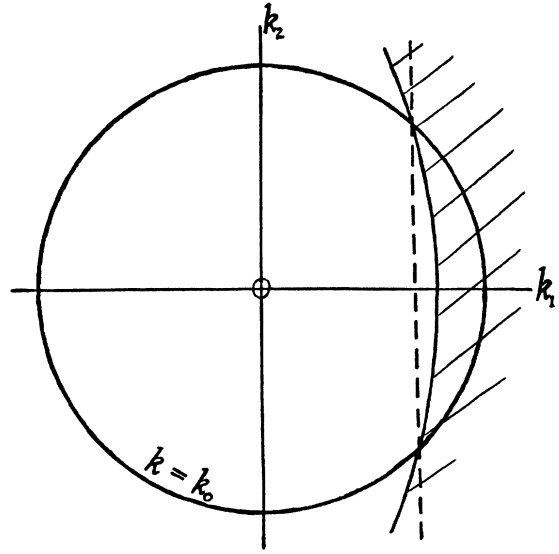


FIG. 1. Region of integration in  $\mathbf{k}$ -space, where  $k_1 > 0, r^2 > 0$ .

where at temperature  $T$

$$|\alpha_k|^2 = \frac{1}{8\pi^3} \frac{dk_1 dk_2 dk_3}{1 + \exp[(E_k - E_0)/\kappa T]},$$

$E_0$  being the energy of the state with  $k = k_0$ ;  $\kappa$  is Boltzmann's constant and  $k_1, k_2, k_3$  are the components of  $\mathbf{k}$  ( $k_1$  normal to the surface and restricted to positive values). The transmission coefficient,  $D(r)$ , is a function of the normal component,  $r$ , of the wave vector of the emitted electron and is zero when  $r^2 < 0$ . From (2),  $r$  is given by

$$r^2 = k_1^2 + \mu(\nu - \nu_k).$$

By integration over all values of  $\mathbf{k}$  we have for the photoelectric current density

$$J(\nu) = \frac{-e}{2\pi^3} \iiint \frac{D(r)X(\mathbf{k}, \nu)dk_1 dk_2 dk_3}{1 + \exp[(E_k - E_0)/\kappa T]}, \quad (4)$$

where the integration is over the volume of  $\mathbf{k}$ -space in which  $k_1 > 0$  and  $r^2 > 0$ . This region is indicated by the shaded area in Fig. 1. In a model in which the electron density and threshold frequency are the same as in ours, but in which the effect of exchange energy is neglected, the curved boundary at the left of the region of integration would be replaced by the broken straight line shown in the figure. Thus we may expect a non-zero value of  $\beta$  to involve a reduction in the magnitude of the photoelectric current.

Now the total energy of the emitted electrons is

$$E = (h/\mu)(r^2 + k_2^2 + k_3^2)$$

and, if  $(h/\mu)r^2 = xE$ , we can transform the integral in (4) to one over  $E$  and  $x$ , giving

$$J(\nu) = \frac{-e}{4\pi} \left(\frac{\mu}{h}\right)^2 \frac{1}{1+\beta} \left[ \int_0^\infty \int_0^1 \frac{D(r)X(\mathbf{k}, \nu)E dx dE}{k_1(1+e^x)} \right], \quad (5)$$

where

$$\chi = (E_k - E_0)/\kappa T = [E - h(\nu - \nu_0)]/\kappa T,$$

$\nu_0$  being the threshold frequency, so that  $h\nu_0 = -E_0$ .

An examination of the formal expression for  $X(\mathbf{k}, \nu)$  given by Makinson<sup>13</sup> reveals that it is approximately independent of the value of  $\beta$ , at least for  $\nu$  near  $\nu_0$ . Near the threshold,  $k_1$  will not differ greatly from  $k_0$ , which is a constant independent of  $\beta$ . Thus the expression in square brackets in (5), which gives the frequency dependence of  $J(\nu)$ , does not depend greatly on the value of  $\beta$ , so that we may expect the photoelectric yield near the threshold to be approximately proportional to the factor  $(1+\beta)^{-1}$ . From Bardeen's results,  $\beta \sim 2$  for sodium, so that this factor can be of considerable significance and should be taken into account in theoretical calculations of the photoelectric yield of metals.

However, the shape of the spectral distribution of the current  $J(\nu)$ , and hence the logarithmic plots of the Fowler method,<sup>2</sup> are to a first approximation independent of the value of  $\beta$ .

This is also the case as shown below for the total and "normal" energy distributions of the emitted electrons, which are determined experimentally by measuring the photoelectric current as a function of the retarding potential between emitting and collecting surfaces.

Measurements of the *total* energy distribution are performed with a spherical collector surrounding a small central cathode, while for the *normal* energy distribution, plane parallel surfaces are employed. If  $U$  is the retarding potential in the former case, the current is given by the Eq. (5) with  $eU$  replacing zero as the lower limit of the integration with respect to  $E$ . In the latter case the expression for the current, when the retarding potential is  $V$ , is obtained from (5) by inserting  $eV$  and  $eV/E$  as the lower limits for the integrations over  $E$  and  $x$ , respectively. It is easily seen that, apart from the constant factors determining their absolute magnitudes, the two expressions obtained in this way are approximately independent of  $\beta$  when the frequency is not far from the threshold. This result was to be expected on physical grounds, since the energy distribution of the emitted electrons is largely determined by their *energy* distribution inside the metal and, unlike the *momentum* distribution, this is independent of  $\beta$ .

Actual computations, appropriate to sodium, have shown that the differences in the distribution functions for the cases  $\beta=2$  and  $\beta=0$  are, in fact, much too small to account for the disagreements with experimental results mentioned earlier, so that the explanation of these discrepancies must be looked for in other directions.

<sup>13</sup> In reference 9,  $U_k(x)$  depends on the momentum of the electron and when operating on  $(u_k + v_k)$  in Eq. (3) of that paper should give  $U_k(x)u_k + U_{k'}(x)v_k$ , where  $k'^2 = q^2 + k^2 + k_x^2$ . In the expressions following that equation,  $U_k(x)$  should be replaced by  $U_{k'}(x)$  and  $q$  redefined so that  $q^2 = r^2 - (\mu/h)U_{k'}(x)$ .

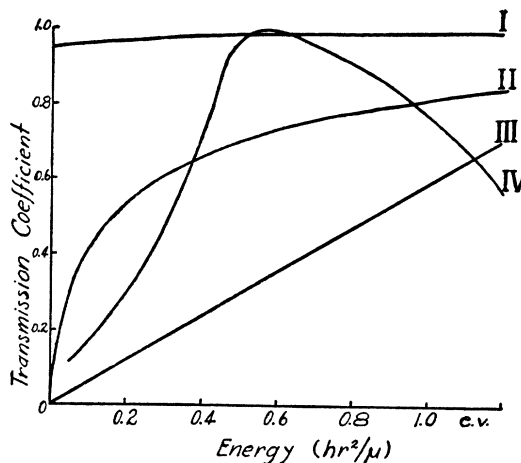


FIG. 2. Transmission coefficient as a function of energy for various potential barriers. (I) Image field barrier, (II) Square barrier, (III) Houston's barrier, (IV) Hill's barrier.

#### IV. THE SURFACE POTENTIAL BARRIER

In the general expression (5) for the photoelectric current, both the factors  $X(\mathbf{k}, \nu)$  and  $D(r)$  depend on the form of the surface potential barrier. As Makinson has shown, however, the excitation function  $X(\mathbf{k}, \nu)$  does not in general vary sharply with  $\mathbf{k}$  or  $\nu$  near the threshold frequency, a fact shown explicitly for the image field and square barriers by the calculations of Hill. Thus, provided  $h(\nu - \nu_0)$  is less than about one electron volt, we shall not be seriously in error if we regard  $X(\mathbf{k}, \nu)$  as constant in performing the integrations in (5).

On the other term,  $D(r)$ , representing the transmission coefficient of the surface barrier, many of the properties of photoelectric emission depend. The fact that experimental results for sodium do not agree with the theory based on an image field barrier has inspired suggestions that the actual barrier has a transmission coefficient that is far from constant.

The transmission coefficient of a number of barriers is illustrated in Fig. 2 as a function of "normal" energy. Measurements of the *total* energy distribution were shown by Hill<sup>7</sup> to require a form of  $D(r)$  with a selective maximum (curve IV), while Houston<sup>10</sup> explained results for the *spectral* and *normal* energy distributions by assuming a coefficient proportional to the normal energy  $(hr^2/\mu)$  and illustrated by curve III in the figure.

Calculations by the present writer have shown that an agreement with experiment, about as close as that found by Houston,<sup>14</sup> can be obtained with the assumption of a square barrier,<sup>15</sup> for which the transmission

<sup>14</sup> See reference 10, Figs. 1 and 2.

<sup>15</sup> The saturation current is then given approximately by

$$J(\nu) \propto (\kappa T)^{5/2} F[h(\nu - \nu_0)/\kappa T],$$

where the function  $F$  is defined by

$$F(x) = \int_0^\infty f(y^2 - x) dy,$$

in which  $f$  is Fowler's function

$$f(x) = \int_x^\infty \ln(1 + e^{-y}) dy.$$

coefficient is approximately proportional to the square root of the normal energy (curve II).

The present inconclusive state of knowledge in regard to the form of the surface potential barrier of sodium is illustrated by the fact that each type of transmission coefficient shown in Fig. 2 has some evidence to support it. Theoretical investigations by Bardeen indicate the image field curve I, while the results of experiment, summarized above, point to one or other of the remaining curves. In view of this uncertainty, experiments performed on the lines suggested in the next section should yield results of considerable value.

### V. PROPOSED EXPERIMENT

Using the arrangement of spherical collector and small central cathode employed in experiments to determine the total energy distribution of emitted electrons, the photoelectric current is measured and plotted as a function of retarding potential,  $E/e$ , for incident light of various frequencies in the vicinity of the threshold. If the relative intensity of the light at different frequencies is measured, the sets of current readings can be adjusted in magnitude so that the value of (incident energy flux/frequency<sup>2</sup>), is the same for each curve. After this adjustment the values of the current,  $J(\nu, E)$ , may be plotted against  $E$  on the same diagram and a point selected on each curve such that the value of  $\chi = [E - h(\nu - \nu_0)]/\kappa T$  is the same at each point. Thus the distance in a direction parallel to the  $E$  axis, between the points on  $J(\nu_1, E)$  and  $J(\nu_2, E)$ , for example, is  $h(\nu_2 - \nu_1)$ . The points so obtained define a curve giving current,  $C_\chi(E)$  say, as a function of  $E$  for a fixed value of  $\chi$ ; after repeating the process for other values of  $\chi$  from about +5 to -10, a family of such curves can be drawn. An example of the type of result to be expected is sketched in Fig. 3.

It is shown below that, for those curves with  $\chi > -1$ , the differential function  $dC_\chi(E)/dE$  is approximately proportional to the transmission coefficient, expressed as a function of  $E$  (compare Fig. 2). Thus

$$D \propto dC_\chi(E)/dE, \quad (6)$$

so that from the experiment described, a direct representation may be obtained of the variation with energy of the surface barrier transmission coefficient.

To establish (6) we note that, since the variation of  $X(\mathbf{k}, \nu)$  and  $k_1$  may be neglected when the frequency is near the threshold, (5) gives approximately,

$$\begin{aligned} J(\nu, E) &\propto \int_E^\infty \int_0^1 \frac{D(r)E' dx dE'}{1+e^{x'}} \\ &= \int_E^\infty (1+e^{x'})^{-1} G(E') dE' \end{aligned}$$

where

$$\chi' = [E' - h(\nu - \nu_0)]/\kappa T$$

and

$$G(E') = \int_0^{E'} D(\{\mu E/h\}^\ddagger) dE = E' \int_0^1 D(r) dx,$$

since  $hr^2/\mu = Ex$ . Integrating by parts,

$$J(\nu, E) \propto (\kappa T) G(E) \log(1+e^{-\chi}) + \dots,$$

where the terms after the first are small for  $\chi > -1$  and  $\kappa T < E < 1$  ev.

Then, when  $\chi$  is kept constant,

$$C_\chi(E) \propto G(E) \log(1+e^{-\chi}),$$

so that

$$dC_\chi(E)/dE \propto D(\{\mu E/h\}^\ddagger) \log(1+e^{-\chi}), \quad (\chi > -1),$$

giving (6).

It is easy to show that, for  $\chi < -3$  and with the same approximations,

$$dC_\chi(E)/dE \propto G(E - \kappa T \chi) - G(E), \quad (\chi < -3),$$

a relation that may be used as a check on results obtained from curves with  $\chi > -1$ .

### VI. CONCLUSION

There are important disagreements between experimental results and the simple theories of photoelectric emission based on a free-electron model with an image field barrier. Near the threshold frequency, the shapes of the observed spectral and energy distributions of photo-electrons from sodium do not agree with the Fowler and DuBridge theories, and it has been shown above that the generalization which includes the effect of exchange forces on the electrons does not improve the agreement.

This generalization does, however, reduce the magnitude of the calculated photoelectric yields of alkali metal surfaces by a factor of about 3, which should help in

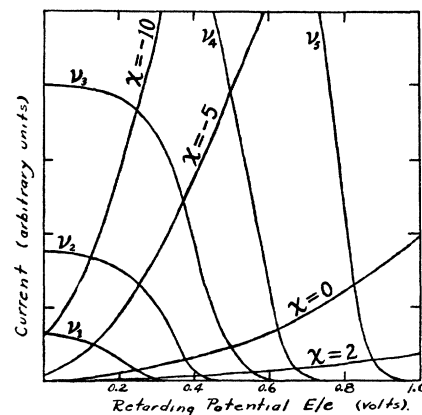


FIG. 3. Current,  $J(\nu, E)$ , versus retarding potential and a possible form for the constant- $\chi$  functions,  $C_\chi(E)$ .

bringing the calculated<sup>16</sup> yields into line with experiment.

The transmission coefficient of the surface barrier is an important factor in the description of photoelectric emission, and experiments such as that described, which could provide definite information on the barrier transmission coefficient, would be of great value, particularly as the special barriers assumed by certain

<sup>16</sup> R. E. B. Makinson, Proc. Roy. Soc. A910, 367 (1937).

authors to explain the normal and total energy distributions are very different, both from each other and from the theoretical barrier for an "ideal" metal.

The writer wishes to record his indebtedness to Dr. R. E. B. Makinson, who suggested this investigation, for many helpful discussions during its progress.

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## The Mechanism of Self-Diffusion in Alkali Metals

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On the basis of calculations of the activation energies of various ring, vacancy, and interstitial mechanisms in alkali metals, the most probable mechanism of self-diffusion is found to be the rapid transmission of short linear regions of compression (referred to as "crowdions") along body-diagonals in the body-centered cubic lattice. The creation of crowdions, which can be regarded as interstitial atoms diluted over a region of about eight interatomic distances in a vernier-like fashion, occurs at the surface rather than in the interior of a perfect lattice. The calculation of the corresponding energy of formation depends on the empirical values for the work function, heat of sublimation, and ionization energy; for sodium, the total heat of activation for diffusion by crowdions is probably less than one-tenth of one electron volt.

### I. INTRODUCTION

**D**IFFUSION in a periodic structure, such as a crystal lattice without macroscopic faults, is presumably the result of a large number of elementary steps from one stable configuration to the next equivalent one. While any elementary mechanism will in general involve the displacement of many atoms in the saddle point configuration (relaxation of neighboring atoms), we may distinguish between elementary steps resulting in the net displacement of one or of several atoms. The former type is only possible if we have either an interstitial atom or a vacancy in the lattice, while an example of the latter process is the cyclic interchange of two or more atoms, which would be the mechanism of self-diffusion in a perfect lattice. The exchange of two neighboring atoms in a metallic lattice is energetically unlikely because of their mutual repulsion. However, Zener<sup>1</sup> suggested that cyclic interchange of more than two atoms in a ring would reduce the activation energy required (due to mutual repulsion). Such steps involving the net displacement of many atoms are not energetically unlikely when the displacements of the individual atoms produce forces aiding the over-all motion. Huntingdon and Seitz<sup>2,3</sup> showed that in the case of copper a vacancy mechanism is probably dominant in accounting for the measured activation energy for self-diffusion.

The alkali metals present a structure which can be approximated by a particularly simple model of positive point charges embedded in a uniform negative charge density. Calculation of the activation energy of various elementary mechanisms in this model can be carried out rigorously involving essentially long-range Coulomb forces. It is found that insertion of an interstitial atom requires much less energy than in the case of copper,<sup>2</sup> where we have neighboring-shell-repulsion to contend with. The energetically favorable interstitial position is not, however, the geometrically obvious face center of the body-centered cubic structure, but between nearest neighbors, the insertion being accompanied by very considerable relaxation displacement along that line of nearest neighbors (forming the stable "crowdion" configuration). The elementary step in the diffusion process involves, then, the net displacement of about eight atoms forming the crowdion,<sup>4</sup> and requires very little activation energy of migration, due to the cooperative action of the several dipoles corresponding to the individual displacements of the ions. Vacancy and ring mechanisms are found to require much higher energies of formation and migration respectively.

The model adopted is a body-centered cubic lattice of positive point charges (each of one electronic charge in magnitude) embedded in a homogeneous negative charge density of constant value balancing the positive

<sup>1</sup> C. Zener, Acta Cryst. 3, 346 (1950).

<sup>2</sup> H. B. Huntingdon and F. Seitz, Phys. Rev. 61, 315 (1949).

<sup>3</sup> F. Seitz, Acta Cryst. 3, 355 (1950).

<sup>4</sup> The term "crowdion" has been coined as a descriptive designation for a short linear region of compression.