Substitution of this into (A1) gives

$$P_{r,\psi,\varphi}\sum_m f_m e^{-im\alpha}=\sum_m e^{-ikr\cos(\psi-\alpha)}e^{im(\varphi-\alpha)}f_m$$

$$=\sum_{mm'}D^{(k)}(r,\psi,\varphi)_{m'm}f_m e^{-im'\alpha}, \quad \text{(A4)}$$

where

$$D^{(k)}(r,\psi,\varphi)_{m'm}=(2\pi)^{-1}\int_0^{2\pi}e^{-ikr\cos(\psi-\alpha)}e^{im(\varphi-\alpha)}e^{im'\alpha}d\alpha$$

$$=(2\pi)^{-1}\int_0^{2\pi}e^{-ikr\cos\beta-i(m'-m)\beta}d\beta \times e^{i(m'-m)\psi+im\varphi}. \quad \text{(A5)}$$

Because of

$$J_n(z)=(2\pi)^{-1}i^{-n}\int_0^{2\pi}e^{-iz\cos\beta-in\beta}d\beta, \quad \text{(A5a)}$$

this differs from the expression given in the text only by the factor $i^{m'-m}$ which can be eliminated by a similarity transformation. It is worth noting that the transition from (17b) to (17c), i.e., the evaluation of the second integral of (17b), can be best carried out using the form (A5a) for J.

A similar calculation is possible also in the three-dimensional case but it is more laborious and will not be given here. It is, essentially, contained in the Appendix to Grosjean's last article.

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Calculated Values of the Parameters of Noble Gas Discharges

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Molar properties of gaseous discharges are determined by the transport cross section which is expressible in terms of the phase shifts defined in electron-atom scattering theory.

$\sigma_t(v)$ was calculated for helium, neon, and argon using values of phase shifts η_0 to η_6 derived by Westin from existing scattering data. Druyvesteyn distribution functions were calculated for E/p from 0.1 to 1.0. Average values were then calculated for collision frequency, drift velocity, diffusion coefficient, and average energy.

Also, collision frequency and elastic energy loss were calculated using Maxwell distributions for kT_e up to 10 ev. These calculations are particularly useful at very low energy, where extrapolation of phase shifts is more reliable than of the experimental data. Values of σ_t are compared with those of Barbiere (taken from direct scattering data); values of drift velocity are somewhat lower than Nielsen's data.

I. INTRODUCTION

THE theory of gas discharges reduces essentially to a study of the various types of collisions which take place among the electrons, atoms, and ions. In many practical cases where the average electron energy is low, the properties of the discharge are determined primarily by the differential cross section $\sigma(k,\vartheta)$ for elastic scattering of an electron by an atom. Here k is the electron wave number, and ϑ the angle through which the electron is deviated.

The ordinary total cross section[1] $\sigma(k)$ is defined by

$$\sigma(k)=\int_0^{\pi}\sigma(k,\vartheta)2\pi\sin\vartheta d\vartheta. \quad (1)$$

In gas discharges, however, since the energy lost by an electron in an elastic collision depends on ϑ, a more important quantity is the transport cross section $\sigma_t(k)$ defined by

$$\sigma_t(k)=\int_0^{\pi}\sigma(k,\vartheta)(1-\cos\vartheta)2\pi\sin\vartheta d\vartheta. \quad (2)$$

(This quantity is also referred to as the diffusion or momentum transfer cross section.) From collision theory, these two cross sections can be expressed[2] in terms of the phase shifts η_n introduced by the atom in the partial waves associated with successive units of angular momentum of the incident electron about the center of the atom:

$$\sigma(k)=\frac{4\pi}{k^2}\sum_{n=0}^{\infty}(2n+1)\sin^2\eta_n, \quad (3)$$

$$\sigma_t(k)=\frac{4\pi}{k^2}\sum_{n=0}^{\infty}(n+1)\sin^2(\eta_n-\eta_{n+1}). \quad (4)$$

Most of the molar properties of the electrons in a discharge, such as drift velocity, diffusion coefficient, etc., are given by some function of σ_t and k, averaged over a distribution function which in turn involves σ_t. Hence, a knowledge of the phase shifts η_n permits calculation of σ_t and this, in turn, enables one to derive the

[1] N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Oxford University Press, London, 1949), Chap. 2.

[2] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) A144, 434 (1933).

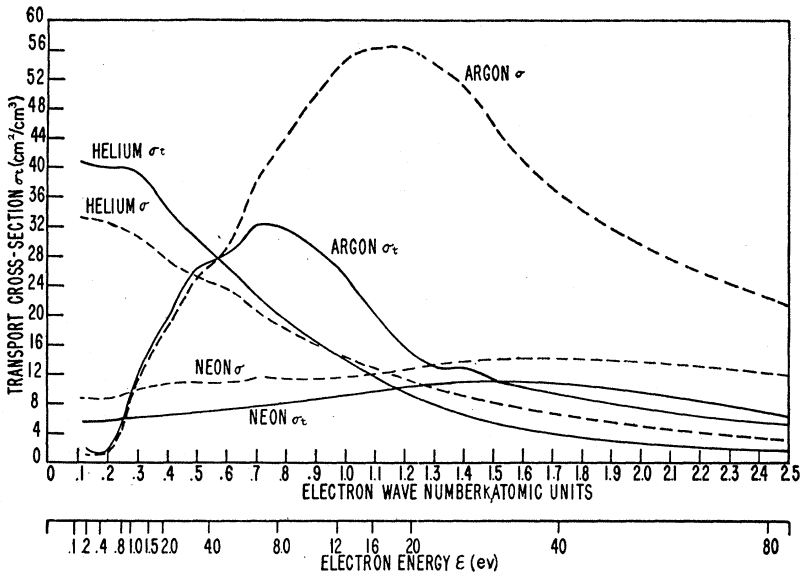

FIG. 1. Transport cross section σ_t as function of electron wave number k, as calculated from phase shifts. The dotted curves are the ordinary total cross sections, σ. Values given refer to pressure of 1 mm Hg, and temperature of 0°C.

various discharge parameters if the distribution function is known. Theoretical calculation of the phase shifts is very difficult, especially at low energies where the Born approximation fails and exchange effects are not negligible. A calculation of σ_t directly from the experimental angular scattering data is possible, but unfortunately scattering experiments become difficult at electron energies of a few ev or less.

II. METHOD OF CALCULATION

Westin[3] in 1946 derived a self-consistent set of phase shifts from experimental data. Voss[4] had shown that mathematical conditions were imposed on the angular scattering distribution curves such that, given an arbitrary angular curve, one could not necessarily reproduce it by some suitable choice of phase shifts. He showed further that the experimental data of Ramsauer and Kollath[5] in argon did not adequately satisfy these consistency conditions for electron energy less than 2 ev or greater than 6 ev. Westin made a thorough compilation of all experimental scattering data available for helium, neon, and argon, and with the aid of a specially-built electromechanical device carried out extensive trial-and-error calculations to find a set of phase shifts best fitting the experimental data.

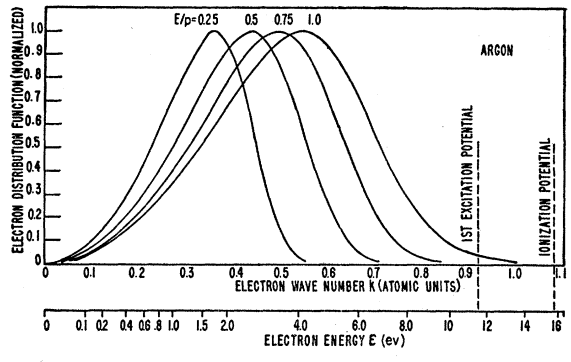

FIG. 2. Generalized Druyvesteyn distribution functions in argon for several values of E/p(volts/cm per mm Hg). Calculations were made using transport cross sections derived from phase shifts.

Values of $\sigma(k)$ and $\sigma_t(k)$ have been calculated for helium, neon, and argon, using Eqs. (3) and (4) and the table of phase shifts given by Westin. His data cover a range of k from 0.2 to 5.0 atomic units. The results are shown in Fig. 1. (All cross sections calculated in this paper are for 0°C. and 1 mm Hg.) The deviation of σ_t from σ is obviously quite marked. Barbiere[6] calculated σ_t directly from the Ramsauer-Kollath scattering data. His values agree almost exactly for neon. For helium they are about 40 percent lower at 2 ev and agree at about 10 ev; and in argon the disagreement is more pronounced, Barbiere's values being about 30 percent lower at low energy and about 100 percent larger at 12.5 volts. The above comparisons are understandable, since the composite scattering data used by Westin for argon deviated appreciably from the Ramsauer-Kollath data, while in helium and neon the difference was much smaller.

These calculated values of σ and σ_t should have particular significance at low energy, because the phase shifts can be extrapolated toward zero energy more reliably than the scattering data. This is true because the scattering theory imposes the restriction that each phase shift equals a multiple of π at k equal to zero. To assign a theoretical value to the cross section at zero

[3] S. Westin, Kgl. Norske Videnskab. Selskab. Forh. No. 2 (1946).
[4] W. Voss, Z. Physik **83**, 581 (1933).
[5] C. Ramsauer and R. Kollath, Ann. Physik **9**, 756 (1931); **10**, 143 (1931); **12**, 837 (1932).
[6] D. Barbiere, Phys. Rev. **84**, 653 (1951).

energy one needs to know the slope of the phase-shift curve.

III. RESULTS FOR DRUYVESTEYN DISTRIBUTION

The velocity distribution function $f(\mathbf{r},\mathbf{v},t)$ for electrons in a gas discharge is given by a solution[7] of the Boltzmann transport equation,

$$\frac{\partial f}{\partial t}=\nabla_v\cdot\frac{e}{m}\mathbf{E}f-\nabla_r\cdot\mathbf{v}f+\frac{\partial f}{\partial t}\Big]_{\text{coll.}}, \tag{5}$$

where ∇_v and ∇_r are the gradient operators in velocity and coordinate space, respectively. In the case of a small uniform dc field E, the solution can be given in the form

$$f=f_0+\frac{\mathbf{v}}{v}\cdot\mathbf{f}_1, \tag{6}$$

where the subscripts refer to a Legendre polynomial expansion in velocity space. By substituting into Eq. (5), and considering only elastic collisions, one obtains the generalized Druyvesteyn distribution for the symmetric part,

$$f_0=A\exp\left(\frac{-3m^3}{M(eE)^2}\int_0^v\sigma_t^2v^3dv\right). \tag{7}$$

Calculations of f_0 have been made for E/p from 0.1 to 2.0 volts/cm per mm Hg in helium, neon, and argon. An example of the influence of the field on the distribution function in argon is shown in Fig. 2. As indicated by the curves, an E/p of much more than 1.0 would indicate an appreciable number of electrons with enough energy to cause inelastic impacts.

The asymmetric term in Eq. (6) can be expressed in terms of f_0 as follows:

$$\mathbf{f}_1=\frac{e}{m}\mathbf{E}\frac{1}{v\sigma_t}\frac{\partial f_0}{\partial v}+\frac{1}{\sigma_t}\nabla_r f_0. \tag{8}$$

The drift velocity $\bar{w}$ for a field E in the x direction is given simply by v_x averaged over $f(\mathbf{r},\mathbf{v})$. By taking $\langle v_xv_y\rangle_{\text{Av}}=\langle v_xv_z\rangle_{\text{Av}}=0$ and $\langle v_xv_x\rangle_{\text{Av}}=\frac{1}{3}v^2$ and using the first term on the right in Eq. (8), one obtains

$$\bar{w}=\frac{4\pi m^2}{NMeE}\int_0^\infty v^5\sigma_tf_0dv, \tag{9}$$

where

$$N=\int_0^\infty f(\mathbf{r},\mathbf{v})d\mathbf{r}d\mathbf{v}.$$

Similarly, by averaging the diffusion current over $f(\mathbf{r},\mathbf{v})$ and using the second term on the right of Eq. (8), one gets for the average diffusion coefficient

$$\bar{D}=\frac{4\pi}{3N}\int_0^\infty\frac{v^3}{\sigma_t}f_0dv. \tag{10}$$

[7] Morse, Allis, and Lamar, Phys. Rev. 48, 412 (1935).

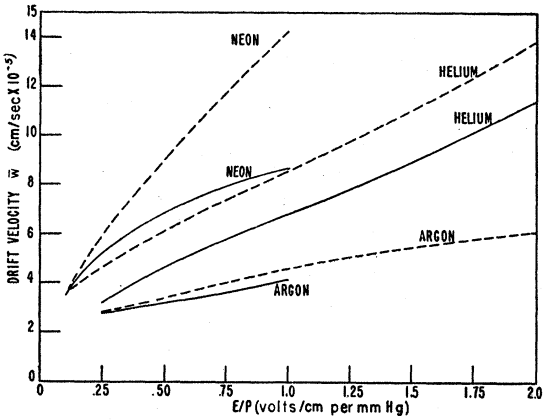

FIG. 3. Drift velocity $\bar{w}$ as a function of E/p. The solid curves are values calculated using phase shifts; the dotted curves are averages taken from Nielsen's experimental data.

By using the above equations and replacing the normalizing factor N by the close approximation $N\cong4\pi\int_0^\infty f_0v^2dv$, the parameters $\bar{w}$ and $\bar{D}$ were calculated for E/p from 0.1 to 1.0 in the three gases. Drift velocity curves are shown in Fig. 3, where the dotted curves are taken from Nielsen's measurements[8] using the electron shutter method. His data are probably the best available. The marked discrepancy in neon is largely due to the fact that for values of E/p greater than 0.25, an appreciable fraction of electrons will have an energy exceeding the excitation and ionization potentials (because of the small cross section for neon). Hence, the distribution function derived assuming only elastic impacts is not very reliable. It might be noted that a theoretical curve of Allen[9] for neon, taking inelastic collisions into account, would lie about half-way between the calculated curve and Nielsen's

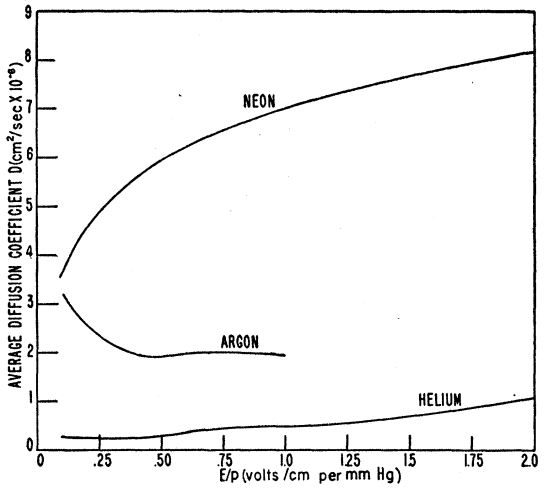

FIG. 4. Average diffusion coefficient $\bar{D}$, for electrons in helium, neon, and argon, as a function of E/p.

[8] R. Nielsen, Phys. Rev. **50**, 950 (1936).
[9] H. Allen, Phys. Rev. **52**, 707 (1937).

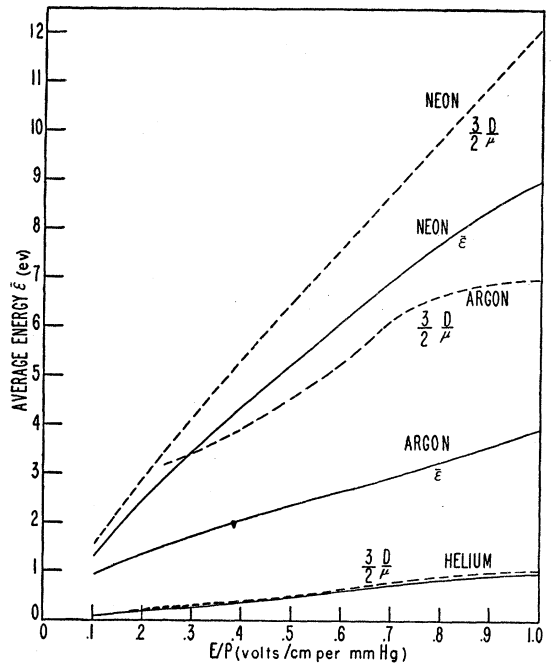

FIG. 5. Average energy of electrons ϵ as a function of E/p, averaging over the generalized Druyvesteyn distribution function. The dotted curves represent average energy as defined by the Einstein relation, where D is the diffusion coefficient and μ the mobility.

curve in Fig. 3. Diffusion coefficient curves are shown in Fig. 4.

The average energy was calculated directly by averaging $\frac{1}{2}mv^2$. It was then compared with the average energy associated with temperature defined by the Einstein relation between mobility and diffusion constant. The results are shown in Fig. 5. The differences arise because the cross sections are not constant, and the distribution functions are not Maxwellian; however, in neon much of the discrepancy at higher E/p is due to inelastic collisions.

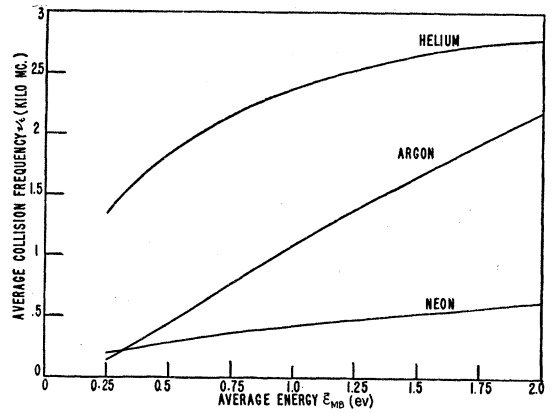

FIG. 6. Average transport collision frequency as a function of average energy assuming a Maxwell-Boltzmann distribution and using transport cross sections derived from phase shifts.

IV. RESULTS FOR MAXWELL DISTRIBUTION

In addition to the above calculations using the Druyvesteyn distribution, a calculation was made of the average transport collision frequency, $\nu_t = v\sigma_t$, averaging over a Maxwell-Boltzmann distribution of various average energies $\bar{\epsilon}_{MB}$ from 0.25 to 2.0 ev. The results are shown in Fig. 6.

Calculations also were made of the average rate of energy loss in elastic collisions, using a Maxwell-Boltzmann distribution for both the electrons and atoms. One can show that the energy loss $\Delta\epsilon$ by an

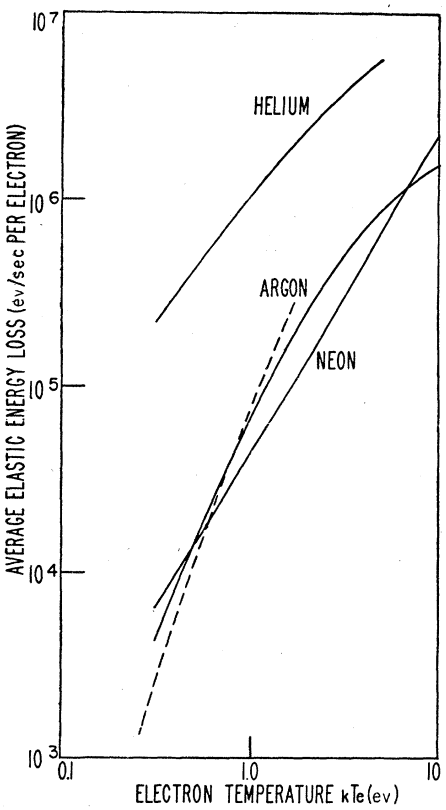

FIG. 7. Average elastic energy loss per electron as a function of electron temperature assuming a Maxwell-Boltzmann distribution for electrons and atoms, and using transport cross sections derived from phase shifts. The dotted curve represents a calculation made by Kenty using the Compton formula and Ramsauer-Kollath cross sections in argon.

electron on elastic collision is given by

$$\Delta\epsilon = \mu_0 \mathbf{V}_0 \cdot (\mathbf{v} - \mathbf{v}'), \tag{11}$$

where $\mu_0 = mM/(m+M)$; $\mathbf{V}_0$ is the velocity of the center of mass, and $\mathbf{v}$ and $\mathbf{v}'$ are the relative velocities before and after impact. This can be reduced to

$$\Delta\epsilon = \mu_0(1-\cos\vartheta)(\mathbf{V}_0 \cdot \mathbf{v}). \tag{12}$$

The rate of energy loss P for a given electron is then

$$P = v\sigma\Delta\epsilon = v\sigma_t\mu_0(\mathbf{V}_0 \cdot \mathbf{v}), \tag{13}$$

and the average rate of energy loss $\bar{P}$ is then

$$\bar{P}=\frac{1}{N_a N_e}\int_0^\infty\int_0^\infty d\mathbf{V}dv v\sigma_t\mu_0(\mathbf{V}_0\cdot\mathbf{v})F_e(v)F_a(V), \quad (14)$$

where $F_e(v)$,N_e and $F_a(V)$,N_a refer to electrons and atoms, respectively.

Values of $\bar{P}$ are shown in Fig. 7, the temperature of the gas atoms being taken as 293°K. The dotted curve is one calculated by Kenty,[10] using the Compton formula,[11] and total cross-section data of Ramsauer and Kollath. He assumed a Maxwell-Boltzmann distribution for the electrons, neglecting the motion of the gas atoms. He also measured the loss experimentally, over a limited range of electron temperature from 0.84 ev to 1.29 ev. His calculated values differed from his experiment by a few percent at the lower temperature and by about 20 percent at the higher temperature. If one makes the comparison using the values of elastic loss per electron derived from the phase-shifts, the agreement is better than 6 percent over the range of Kenty's experimental values.

[10] Kenty, Easley, and Barnes, J. Appl. Phys. **22**, 1006 (1951).
[11] K. T. Compton, Phys. Rev. **22**, 333 (1923).

V. DISCUSSION

The probable accuracy of these calculations is estimated to be within 10 percent for electron energy greater than 0.15 ev. The main source of error lies in the original set of phase shifts. A direct comparison with theoretical calculations is possible only for helium. The zero-order phase shift for helium used in these calculations agrees very closely with a calculation by Morse and Allis[12] using a Hartree field, and also with a recent calculation by Moiseiwitsch[13] using a variational method. For $k<1.0$ (13.5 ev) the agreement among the three is about 1 percent; and for $k<2.5$($\sim$85 ev) the agreement is better than 6 percent.

There are two features of significance in these phase shift calculations. First, the extrapolation of phase shifts to energies less than 1 or 2 ev is probably more reliable than extrapolation of the direct scattering data. Second, the transport cross sections constitute a central set of data from which many discharge parameters can be calculated; thus, if experimental agreement is established for several parameters, then one can more confidently extend the calculations to parameters which are not easily measured accurately.

[12] P. M. Morse and W. P. Allis, Phys. Rev. **44**, 269 (1933).
[13] B. L. Moiseiwitsch, Proc. Roy. Soc. (London) **A219**, 102 (1953).

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Ionic Conductivity of Impure Polar Crystals*

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Experimental determinations of the ionic conductivity of impure or "doped" alkali halide crystals are often used to find the mobility of the cation vacancies. For this purpose it is important to know to what extent the vacancies and the impurity ions have associated together to form neutral "complexes," which do not contribute to the conductivity. Previous interpretations of the experimental data have relied largely on the law of mass action to give the degree of association, but have neglected the long-range Coulomb interactions between the unassociated impurity ions and vacancies. The effect of these interactions on the calculated degree of association and upon the dc conductivity is examined in this paper. The interactions are shown to be significant even in systems containing impurities in concentrations of no more than one part in 10^4. A new analysis of the results obtained by Etzel and Maurer for the system $NaCl+CdCl_2$, leads to a binding energy of about 0.35 ev for the cadmium ion-vacancy complex. The mobility of the sodium ion vacancy is found to be about 30 percent larger, at all temperatures, than was inferred by Etzel and Maurer, using a simpler theory to interpret the data. The activation energy for the vacancy motion remains however at about 0.9 ev.

I. INTRODUCTION

THE ionic conductivity of polar crystals has in recent years engaged the attention of many investigators. The earlier work, mainly on pure crystals, has been reviewed by Mott and Gurney[1] and by Seitz.[2] More recent reviews have been given by Jacobs and Tompkins,[3] and by Jost.[4]

In general the ionic current is carried by the migration of lattice vacancies and interstitial ions. The analysis of the experimental data is complicated by the temperature dependence not only of the numbers of the various carriers but also of their mobilities. Thus the

* This work was supported by the U. S. Office of Naval Research.
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[1] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, Oxford, 1948), Chap. II.
[2] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. XV.
[3] P. W. M. Jacobs and F. C. Tompkins, Quart. Revs. London **6**, 238 (1952).
[4] W. Jost, *Diffusion in Solids, Liquids, Gases* (Academic Press, New York, 1952), Chap. IV.