

F<sub>IG</sub>. 2. The effect on the deformation-induced charge flow of removing and reapplying a load increment. The loading schedule is indicated by the heavy line at the top of the diagram. The current in amperes may be obtained by multiplying the deflection are related by  $E^* = E(1 \pm \Delta)$ . (2)<br>by  $5 \times 10^{-15}$ .

at jogs,<sup>3</sup> and since the energy of formation of a positive ion vacancy is probably less than that of a negative ion vacancy,<sup>4</sup> it follows that plastic flow should produc positively charged dislocations and leave behind in the lattice a net excess of (negatively charged) positive ion vacancies. When the deformation is inhomogeneous, it is then reasonable that the side on which the stress is concentrated develop a negative charge, as observed, since the positive dislocations move into the crystal, leaving behind negatively charged vacancies.

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<sup>1</sup> A. W. Stepanow, Physik. Z. Sowjetunion 4, 609 (1933).<br><sup>2</sup> F. Seitz, Revs. Modern Phys. 23, 328 (1951).<br><sup>3</sup> F. Seitz, Phys. Rev. **79**, 1002 (1950); 80, 239 (1950).<br><sup>4</sup> N. F. Mott and M. J. Littleton, Trans. Faraday Soc.  $(1938).$ 

## Self-Diffusion and Ionic Conduction in Crystals

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HE coefficient of self-diffusion D and the ionic conductivity  $\sigma$  of ionic crystals, both referring to one type of transport mechanism, are customarily related by the Einstein relation

$$
\sigma/D = Ne^2/kT,\tag{1}
$$

where  $N$  is the number of ions of a given kind,  $e$  the electron charge,  $T$  the absolute temperature and  $k$ Boltzman's constant.

If the carrier of the ionic current is capable of forming electrically neutral aggregates with another imperfection (for example, with vacancies of opposite sign or divalent ions) then these neutral aggregates cannot con-

tribute to the conductivity but they may contribute appreciably to the self-diffusion. In such cases deviations from (1) may be expected (and have been found) such that  $\sigma/D\!<\!N e^2/kT$ .<sup>1</sup>

Recently a careful study on AgCl yielded an example where  $\sigma/D > Ne^2/kT$ . The purpose of the present note is to point to a probable explanation of this type of deviation from (1).It is based on a correction which must be applied to the customary derivations of  $(1)^3$ in the case of dielectrics.

The force which an external electric potential difference  $V$ , applied across a crystal of length  $l$ , exerts on a charge e inside a polarizable medium is not  $eV/l=eE$ , but greater. The effective field  $E^*$  and the field  $E=V/l$ are related by

$$
E^* = E(1 \pm \Delta). \tag{2}
$$

If the charge carrier is assumed to be a sphere with dielectric constant  $\epsilon_1$  in a homogeneous medium of dielectric constant  $\epsilon_0$ , then

$$
\Delta = \epsilon_1(\epsilon_0 - 1)/(2\epsilon_0 + \epsilon_1). \tag{3}
$$

Equation (2) leads straightforward to a generalized Einstein equation for dielectrics:

$$
\sigma/D = Ne^2(1+\Delta)/kT > Ne^2/kT.
$$
 (4)

Equation (4) qualitatively explains the discrepancy observed by Compton and Maurer for AgC1. The conditions under which Eq. (3) is valid are not well satisfied for a conducting ionic vacancy or interstitial ion, so that (3) is only a rough approximation of the true value of  $\Delta$ . Because the polarization on an atomic scale is not homogeneous and the path of the vacancy or interstitial ion avoids places where the polarization is high, it is reasonable to multiply the right side of (3) by a correction factor of the order  $\frac{1}{2}$ . We shall now discuss two typical cases: AgC1 and NaBr. For interstitial ions the dielectric constant will be taken equal to the dielectric constant of the material since their contribution to the over-all dielectric constant is greatest by far. Thus one expects for interstitial ions for AgCl  $(\epsilon = 12)$   $\Delta = 1.85$  and for NaBr  $(\epsilon = 6)$   $\Delta = 0.84$ .

For vacancies one may either take  $\epsilon_1 = 1$ , yielding for AgCl  $\Delta$ =0.22 and for NaBr  $\Delta$ =0.19, or one may make an estimate of  $\Delta$  with  $\epsilon_1 = \epsilon_0$  by considering the motion of the ion jumping into the hole. This ion moves through the central part of a region with an extremely low polarization field exerted by other Ag<sup>+</sup> ions. Depending on which of several crude approximations one uses, he finds that this field is from 10 to 25 times as weak as that through which an interstitial ion moves, leading to  $0.19 > \Delta > 0.08$  for AgCl and  $0.1 > \Delta > 0.04$ for NaBr.

The essential conclusion of this crude analysis is that for vacancy transport  $\Delta$  is so small that it may well have escaped detection but for interstitial transport, especially for ionic crystals with high dielectric constant,  $\Delta$  will be appreciable. This affords a new criterion for deciding whether electrolytic transport takes place interstitially or by vacancies. The fact that for NaBr  $\Delta$  was found to vanish within the accuracy of the experiments' supports the vacancy transport assumption for this material. The fact that for AgCl  $\Delta$ was found experimentally' to range between 1 and 2 is strong support for the interstitial transport assumption for the silver salt.

' See for example H. W. Schamp and E. Katz, Phys. Rev. 94,

828 (1954).<br>
<sup>2</sup> W. D. Compton, doctoral thesis under R. J. Maurer, University of Illinois, Urbana, Illinois, 1955 (unpublished).<br>
<sup>3</sup> See for example N. F. Mott and R. W. Gurney, *Electronic* 

Processes in Ionic Crystals (Oxford University Press, Oxford, 1940), p. 63.

## Outgoing and Ingoing Waves in Final States and Bremsstrahlung\*

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 'T is well known that, in calculating transition probabilities between stationary states, a scattered particle in the final state should be represented by a wave function whose asymptotic form is plane wave plus ingoing spherical wave, rather than by the usual scattering wave function. The importance of this point has been stressed repeatedly, and in particular in connection with the recent calculation of bremsstrahlung at high energies.<sup>1</sup>

On the other hand, it has been pointed out<sup>2</sup> that this particular choice of 6nal state wave functions is only required if the differential cross section for a given direction of the scattered particle (final electron in the case of brernsstrahlung) is to be calculated. If it is asked for the cross section integrated over the direction of the scattered particle, then one can equally well use the outgoing wave type of wave function for the final state. This may be understood from the fact that in this case the direction of motion of the scattered particle merely represents a degeneracy of the final state. One may therefore use any complete set of states to represent the particle; in particular the outgoing wave modification may be chosen.

In the bremsstrahlung problem, these statements hold if the total cross section for emission of a quantum of a given energy and direction is desired. Ke need in this case a complete set of wave functions for the electron of a given energy. The statement that outgoing waves may be used for the electron will now be proved explicitly for a Dirac electron in a spherical symmetric potential.

Let  $\psi_+{}^{\mu}(\mathbf{p}, \mathbf{r})$  denote the Dirac wave function with asymptotic form: plane wave with momentum p together with  $\begin{pmatrix} \text{out} \\ \text{in} \end{pmatrix}$ -going spherical wave,  $\mu$  being the spin label. In an arbitrary coordinate system this can clearly be written as

$$
\psi_{\pm}{}^{\mu}(\mathbf{p}, \mathbf{r}) = \sum_{j j_z l m} i^{l} \langle j j_z | l m_{\frac{1}{2}\mu}^{\frac{1}{2}} \rangle \times Y_{l, m}{}^{*}(\mathbf{p}/p) e^{\pm i \delta l, i \Phi_{l j j_z}(\mathbf{r})}, \quad (1)
$$

where  $Y_{l,m}$  are the spherical harmonics,  $\langle jj_z | lm_z^2 \mu \rangle$  the Clebsch-Gordan coefficients,  $\delta_{l,j}$  the phases and  $\Phi_{l j j z}$ the standing wave solutions

$$
\Phi_{ijj_{z}}(\mathbf{r}) = 4\pi \left(\frac{E+m}{2E}\right)^{\frac{1}{2}} \left[\frac{\frac{\hat{p}}{E+m}f_{l,\ j}(r)(\sigma\mathbf{r}/r)\chi\,_{ij_{z}}}{g_{l,\ j}(r)\chi\,_{ij_{z}}}\right],
$$

 $\chi_{ij}$  being the central field spinors,<sup>3</sup> and  $f_{l, j}$  and  $g_{l, j}$  the usual radial functions with asymptotic behavior:

$$
f_{l,j}(r) \rightarrow (1/pr) \cos(pr - \frac{1}{2}l\pi + \delta_{l,j}),
$$
  

$$
g_{l,j}(r) \rightarrow (1/pr) \sin(pr - \frac{1}{2}l\pi + \delta_{l,j}).
$$

The probability for a process described by a perturbation 8, integrated over angles and summed over spins in the final state, is proportional to

$$
I_{\pm} = \sum_{\mu = \pm \frac{1}{2}} \int d\Omega_{p_f} \left| \int d^3 r (\boldsymbol{\psi}_{\pm}{}^{\mu})^{\dagger} (\mathbf{p}_f, \mathbf{r}) \, \Theta \boldsymbol{\psi}_i \right|^2. \tag{2}
$$

On account of the orthogonality of the spherical harmonics and of the Clebsch-Gordan coefficients, the factor  $\exp(\pm i\delta_{l, i})$  depending upon the choice of out- or ingoing wave modifications, disappears from the expression

$$
I_{\pm} = \sum_{l \, j \, i} \left| \int d^3 r \Phi_{l \, j \, j}^{\dagger}(\mathbf{r}) \, \Theta \psi_i \right|^2, \tag{3}
$$

giving the matrix element in terms of standing waves.

Turning now to the bremsstrahlung, it will be seen that the present remark introduces considerable simplifications:

Although it is necessary to use the final state wave function  $\psi$ <sup>*f*</sup> in order to obtain the correct differential cross section, ' it is now clear that as soon as the cross section is integrated over angles of the electron, we can forget about the difference between  $\psi$ <sup>*f*</sup> and  $\psi$ <sub>+</sub><sup>*f*</sup>. We may therefore take advantage of using  $\psi_+$  in the final state, and hence we can deduce the bremsstrahlung cross section integrated over angles of the electron from the corresponding pair cross section by the familiar transformations  $d\epsilon_1/k^3 \rightarrow dk/kp_1^2$  and the change of sign of  $p_2$  and  $\epsilon_2$ . This conclusion holds whether the screening is absent, partial or complete. In particular