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Electron transport in the bulk photovoltaic effect

H. Heyszenau
I. Institut für Theoretische Physik, Universität Hamburg, D-2000 Hamburg 36, Germany

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The spontaneous motion of electrons in the bulk photovoltaic effect in pyroelectric materials may be explained by separating the processes into two steps: the generation of photoelectrons whose distribution is asymmetric in momentum and a subsequent normal diffusion of the carriers. Asymmetric generation violates time-reversal symmetry and is shown to be only possible for local states in polar systems. Transport properties are calculated for the short-circuit and the open-end case. It is shown that in high-resistivity materials the short-circuit current is not affected by impurities other than those supplying the asymmetric photoelectrons. The open-end saturation field is proportional to the short-circuit current $E_s = J_{sc}/\sigma$, where σ is the photoconductivity. Both results agree with experiment.

I. INTRODUCTION

Some ferroelectrics like $LiNbO_3$, $LiTaO_3$, $BaTiO_3$, etc., change their index of refraction under illumination. Early attempts to explain this "optical damage" or "bleaching" attributed it to a diffusion of photoexcited carriers out of the illuminated into the dark regions. The resulting carrier-density profile then in turn induces a local variation of the optical properties. Extensive experiments confirmed in principle the migration of carriers between light and dark regions, however, they showed that the process is more complicated than simple diffusion.[1-3] Homogeneous illumination of a single-domain crystal gives rise to a field of the order of 10^5 V cm^{-1} along the c axis, which means that carriers are being transported spontaneously in a well-defined direction, piling up at the end of the domain. This picture is further substantiated by the fact that by contacting the ends of the domain, short-circuit currents proportional to the light intensity may be drawn without external electric field. The dependence of this current on wavelength and polarization of the incoming light is not proportional to the optical density, indicating that only carriers originating from particular transitions contribute to this effect. (In $BaTiO_3$ the direction of the current may be reversed by altering the polarization of the incoming light.[4])

This spontaneous motion of photoelectrons in the entire volume of a substance is called the bulk photovoltaic effect (BPVE) and is of practical interest for the storage of volume holograms.[1,5]

The microscopic processes giving rise to the BPVE are not yet fully understood in spite of a large amount of experimental information. In particular it is still unclear whether the spontaneous transport of carriers is intrinsically connected to impurities or whether it results from properties of the pure substance, possibly enhanced by impurity effects.

Experiments on $LiNbO_3$ suggest a very strong connection to impurities. It is found that the bulk photovoltaic efficiency κ defined by[2]

$$J_{sc} = \kappa \alpha I \,, \tag{1}$$

where J_{sc} is the external short-circuit current, α the optical density, and I the light intensity, shows a pronounced correlation to doping in absolute value and spectral dependence.[6,7] In particular, concentrations of some 10^{-4} Fe give extremely high efficiencies, and in addition it is found that the spectral dependence of κ corresponds to a $Fe^{2+} \rightarrow Nb$ transition in the absorption spectrum.[2] Finally the current is proportional to the content of Fe^{2+} ions over a wide range of concentrations.[6] In spite of this strong correlation between the BPVE and impurities in $LiNbO_3$ the situation is less clear if one takes into account that in other substances like $BaTiO_3$ the same effect takes place in nominally pure crystals[4] and that it may also be found in pure $LiNbO_3$ by two-photon excitation.[8]

The experimental results mentioned above would be compatible in principle with a model attributing the transport to the bulk system and assuming that the impurities merely supply the carriers. In Sec. II we show, however, that symmetry arguments lead to a crucial importance of the localized states for the transport process itself. It must then be assumed that in the pure system defects play the role of impurities, for which there seems to be some experimental evidence.[9] The alternative possibility of asymmetric polaronic motion within the conduction band will not be considered here as it is not clear at the moment whether the energies in question are compatible with this model.

The microscopic processes responsible for the BPVE may be qualitatively divided into two steps. First, the photoexcited electron must possess some initial momentum in a well-defined direction with respect to the polar axis, and second, it must move in this preferred direction over macroscopic

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distances in order to contribute to the external short-circuit current. Recently several models have been proposed which rely on the formation of local time-dependent dipoles and calculate the current as the averaged time derivative of the dipole moment. It is clear that such processes can only contribute to current fluctuations and do not give rise to a steady external current.

A system which gives spontaneous photocurrents was studied by Neumark[10] in connection with experiments on laminated ZnS crystals. These crystals may be represented as a sequence of junctions whose photovoltages accumulate if at least one of the components has no center of inversion. This model also explains photovoltages due to the grain boundaries in polycrystalline samples of pyroelectrics. It cannot be applied to the case of impurities in $LiNbO_3$ as it would require the impurities to form some sort of lamination for which there is no evidence.

II. SYMMETRY

The existence of a spontaneous electric current requires states of opposite momentum to be inequivalent and thus clearly breaks time-reversal symmetry. Excluding electron-phonon interactions for the moment, we may show that the BPVE cannot occur for symmetry reasons in a pure Bloch state but must be due to localized states.

It is evident from experiments that magnetic effects play no role and thus the Hamiltonian itself is time-reversal invariant. The breaking of symmetry is then due to the boundary conditions.

Bloch states of opposite momentum are connected in the undisturbed crystal by the time-reversal operator K

$$K\psi_{\vec{k}}(\vec{x}) = \psi_{-\vec{k}}(\vec{x}) = \psi^*_{\vec{k}}(\vec{x}) \tag{2}$$

(where spin has not been taken into account explicitly for symmetry reasons) and are thus degenerate irrespective of the symmetry group of the crystal. The matrix element for photoexcitation from state $\psi_{\vec{k},v}$ of momentum k in the valence band to state $\psi_{\vec{k}c}$ in the conduction band is

$$M_{\vec{k}v,\vec{k}c} \sim i\vec{E} \int d^3x\, \psi^*_{\vec{k}v}(\vec{x}) \nabla \psi_{\vec{k}c}(\vec{x}) , \tag{3}$$

where $\vec{E}$ is the electric-field vector of the incident light. From condition (2) we have

$$M_{\vec{k}v,\vec{k}c} = -M^*_{-\vec{k}v,-\vec{k}c} , \tag{4}$$

and thus

$$|M_{\vec{k}v,\vec{k}c}|^2 = |M_{-\vec{k}v,-\vec{k}c}|^2 . \tag{5}$$

The states $\psi_{\vec{k},v}$ and $\psi_{-\vec{k},v}$ being degenerate are equally populated. Due to (5) this is also true for $\psi_{\vec{k},c}$ and $\psi_{-\vec{k},c}$ upon photoexcitation and the net current of photoelectrons vanishes. This statement remains valid if additional interactions are introduced as long as they do not break time-reversal symmetry. We have, therefore, no asymmetry in momentum distribution in a system of pure Bloch states.

The situation is different if we allow for defects. In addition to a possible bound state the conduction band is then disturbed and we must construct a continuum state from the Bloch functions. The boundary conditions are analogous to those used for the photoionization of atoms where the proper choice was shown[11] to be an incoming spherical and an outgoing plane wave. In our case this reads

$$\phi^{(-)}_{\vec{k}}(\vec{x}) = \psi_{\vec{k},c}(\vec{x}) + \int d^3\vec{x}\, G^{(-)}_{\vec{k}}(\vec{x},\vec{x}')V(\vec{x}')\phi^{(-)}_{\vec{k}}(\vec{x}') , \tag{6}$$

where $\psi_{\vec{k},c}$ is the conduction band Bloch function, $V(\vec{x})$ is the scattering potential of the impurity or defect, and

$$G^{(\pm)}_{\vec{k}}(\vec{x},\vec{x}') = \lim_{\delta \to 0} \int d^3\vec{k}'\, \frac{\psi^*_{\vec{k}',c}(\vec{x})\psi_{\vec{k}'c}(\vec{x})}{E_{\vec{k}} - \epsilon_{\vec{k}'} \pm i\delta} \tag{7}$$

is the Green's function for incoming (–) and outgoing (+) "spherical" waves. $\epsilon_{\vec{k}}$ is the band energy of the electrons and $E_{\vec{k}}$ the energy of the continuum state.

Time reversal, being equivalent to complex conjunction, now gives

$$K\phi^{(-)}_{\vec{k}}(\vec{x}) = \phi^{(+)}_{-\vec{k}}(\vec{x}) , \tag{8}$$

which contains an outgoing Green's function and is thus excluded by the boundary conditions which only allow for incoming "spherical" waves as mentioned above. The state of opposite momentum $-\vec{k}$ is connected to $\phi^{(-)}_{\vec{k}}$ by the inversion operation I

$$\phi^{(-)}_{-\vec{k}}(\vec{x}) = I\phi^{(-)}_{\vec{k}}(\vec{x}) , \tag{9}$$

provided I is an element of the symmetry group. Otherwise the states $\phi^{(-)}_{-\vec{k}}$ and $\phi^{(-)}_{\vec{k}}$ are independent and give in general different probabilities of photoexcitation from the localized state into continuum states of opposite momentum. The connections of the four states belonging to momenta $\vec{k}$ and $-\vec{k}$ are summarized in Fig. 1 where the ones in the upper line are allowed by the boundary conditions.

The absence of inversion symmetry is a necessary condition for the existence of a spontaneous external current but is it not yet sufficient. In most crystals without inversion symmetry one still has pairs of defect sites which are equivalent apart from having opposite orientation. Even if each one is capable of emitting a directed current of electrons, these compensate and there is no macroscopic net current. Thus we must impose

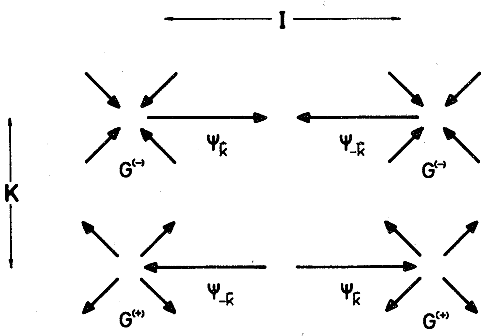

FIG. 1. Transformation of the continuum states of plane-wave momenta $\vec{k}$ and $-\vec{k}$ under inversion I and time reversal K.

the additional requirement that the asymmetry in all equivalent sites has the same sense, which means that we need a polar axis in the crystal.

Summing up we find that the asymmetry requirement for obtaining a net spontaneous photocurrent is (a) a polar axis in the host crystal and (b) the existence of "local" states in the sense that these states do not have the full translation symmetry of the lattice. (They may still be extended and in fact are in this case.) All these requirements are fulfilled by defects in pyroelectric and ferroelectric crystals.

This far breaking of time-reversal symmetry was assumed to be due to the local boundary conditions of rigid continuum states. Including relaxation effects of the lattice we obtain in addition the possibility that time-reversal symmetry is broken thermodynamically by the heat bath. This effect gives rise also to anisotropic initial momentum and will be treated in a subsequent paper.

III. CONDITIONS FOR DIRECT CURRENT

In Sec. II we studied the symmetry requirements for directed emission of electrons from impurities upon photoexcitation. The next step consists in considering under what conditions these electrons contribute to direct current which may be measured at the boundaries of a macroscopic system. Microscopically this means that we must have momentum correlation over infinite distances, or in other words, the electron must move in some preferred direction through the entire crystal. It may seem that this requirement has been fulfilled in Sec. II by taking the wave function according to Eq. (6) as there is an outgoing wave traveling freely over infinite distances. The situation is, however, not trivial as we have until now neglected the presence of other impurities or defects and, in particular, of those which do not take part in the photoexcitation mentioned above. As soon as the electron is scattered (i.e., in the distance of the order of a mean-free path) its momentum is randomized and it does no longer contribute to the external current. This problem does not arise in normal field conduction as there the carrier is accelerated by the external field and thus reacquires its preferred direction after each scattering.

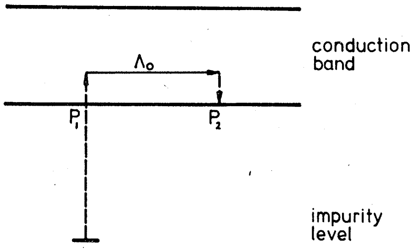

FIG. 2. Electron motion in asymmetric photoexcitation.

In the absence of external fields a similar effect might be imagined assuming that the electric current is carried by electrons which so to speak jump from one "active" impurity to the other thus being reaccelerated every time. The relevant parameter of this model being the distance between the impurities gives a nonlinear dependence of the current on impurity concentration while experiments clearly show linear dependence over a wide range of concentrations.[7] Direct transitions between impurities may thus be excluded as the main driving mechanism. For low impurity concentrations the distance between centers is large as compared to the mean free path of the emitted electrons and each center is independent of the others.

Let us consider the situation where an electron which was emitted asymmetrically from an impurity, is being scattered after moving the average distance of the mean free path. There are now three forces acting on the carrier: (a) the attractive force of the hole it left behind, (b) the macroscopic field possibly present in the crystal, and (c) a "concentration gradient" which will be discussed below. The first two forces clearly act against the BPVE which requires the electron to leave the impurity and to move against the macroscopic field.

A schematic sketch of the emission process is given in Fig. 2. The motion of carriers may be divided into two distinct parts. (i) After being excited at point P_1 the carrier moves a certain distance Λ_0 before being scattered inelastically at P_2. This motion takes place at some energy above the lower edge of the band (some tenth of an eV according to experiments) and is asymmetric as discussed before. (ii) There is a diffusion current with mobility μ at the bottom of the band. ("Band" means a region of finite density of states rather than a band in the Bloch sense.) It must be kept in mind that Λ_0 is not the mean-free path belonging to μ as these parameters belong to different energies.

Considering for the moment the short-circuit case where there is no macroscopic field present we find that the time dependence of the process we are studying is governed by two characteristic times (i) the time constant of emission of electrons from the impurity defined by

$$\tau_e = 1/W_e = 1/\alpha\gamma I\,, \tag{10}$$

where W_e is the emission probability per unit time, α is the optical density, I the light intensity, and γ a factor which gives the fraction of excited electrons going into the state of asymmetric momentum. (ii) The time the electron needs to return under the local field and to neutralize the disturbance depends on the bulk conductivity of the crystal and is given by

$$\tau_r = \Lambda_0^3 \epsilon / e^2 \mu\,, \tag{11}$$

where μ is the mobility in the conduction band, Λ_0 the mean-free path of the emitted electrons, and ϵ the dielectric constant of the specimen.

In case $\tau_e > \tau_r$ the charge disturbance is being neutralized before the next electron is emitted. The entire process then essentially involves one single particle building up a dipole and returning again to the impurity. This process does not contribute to the BPVE as mentioned above, as the carrier does not separate from the impurity which is necessary for contributing to the direct external current.

Let us now consider the case where $\tau_e < \tau_r$, i.e., the "returning time" of electrons is larger than the time interval between emissions. In this case there is still some part of the dipole left by the time the next electron is being emitted. We then obtain a *stationary* nonequilibrium state which will be shown in Sec. IV to carry external direct current.

IV. MOTION OF CARRIERS

Taking account of the fact that the substances under consideration have low mobility we use a diffusion-type formalism for describing the motion of the carriers. For simplicity we assume that only electrons contribute to the BPVE and that the holes are practically immobile. There is some reason to believe that the valence bands consisting primarily of oxygen orbitals are rather narrow. If in a particular case this assumption is not valid, then the following arguments remain quite the same apart from the fact that the corresponding equations for holes must be included.

The probability of finding an electron at point $\vec{x}$ at time t is $\rho(\vec{x}, t)$ whose time dependence is governed by Smoluchowski's equation of diffusion.[12]

$$\frac{\partial\rho(\vec{x},t)}{\partial t} = \mathrm{div}[\mu\vec{E}\rho(\vec{x},t) + D\,\mathrm{grad}\rho(\vec{x},t)] + Q(\vec{x}) - R(\vec{x})\,. \tag{12}$$

(This equation is obtained from the more familiar Fokker-Planck equation in the large damping case when local thermal equilibrium is established instantaneously). Here D is the diffusion constant which depends on the mobility through Einstein's relation

$$D = \mu k T\,. \tag{13}$$

$\vec{E}$ is the local electric field, $Q(\vec{x})$ is the local rate of generation, and $R(\vec{x})$ of recombination of carriers. Generation and recombination contain interband parts and contributions from the impurity. We will at present not consider the interband parts assuming that the carrier lifetime with respect to bulk electron-hole recombination is long as compared to the time constant of the processes under consideration. This assumption allows again for omitting the continuity equation for the holes and correspondingly we only take into account the impurity contributions in $Q(\vec{x})$ and $R(\vec{x})$.

$Q(\vec{x})$ is the number of photoexcited electrons arriving directly from the impurity at point $\vec{x}$ via the asymmetric process. $R(\vec{x})$ describes the "refilling" of the ionized impurity. The values of $Q(\vec{x})$ and $R(\vec{x})$ depend on the local environments of the impurity and require knowledge of the continuum states Eq. (6). Figure 3 shows the qualitative behavior of Q and R along the c axis in the vicinity of an impurity at z_i. Recombination is only appreciable within the range of the localized wave function of the impurity. Photogeneration Q is asymmetric and its main peak is in the forward direction and lies in the distance of the mean-free path of the emitted carriers Λ_0.

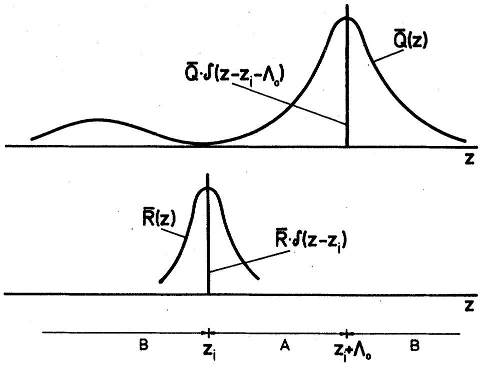

FIG. 3. Rates for trapping of photoelectrons $Q(z)$ and of recombination $R(z)$ in the vicinity of an impurity at z_i. The symbols are explained in the text.

The local electric field $\vec{E}$ in (12) is connected to the charge disturbance by Poisson's equation and introducing the potential function

$$\vec{E}(\vec{x}) = -\nabla\psi(\vec{x}) , \tag{14}$$

we have

$$\Delta\psi(\vec{x}, t) = (e^2/\epsilon\epsilon_0)[\rho(\vec{x}, t) - \bar{\rho}] , \tag{15}$$

where $\bar{\rho}$ is the carrier density in the neutral bulk and ϵ its dielectric constant.

Assuming that the system is in local thermal equilibrium we may introduce the electrochemical potential $\varphi(\vec{x}, t)$ which is connected to the density by the relation

$$\rho(\vec{x}, t) = \rho_0 e^{-\beta[\varphi(\vec{x}, t) - \psi(\vec{x}, t)]} , \tag{16}$$

where $\beta = (kT)^{-1}$.

The condition for a stationary state of (12) is

$$(1/e)\,\mathrm{div}\vec{j}(\vec{x}) - Q(\vec{x}) + R(\vec{x}) = 0 , \tag{17}$$

where we have introduced the local current

$$\vec{j}(\vec{x}) = e\mu\rho(\vec{x})\,\mathrm{grad}\varphi(\vec{x}) . \tag{18}$$

Inserting (16) and (18) into (15) and (17) we obtain the two coupled nonlinear differential equations

$$\mathrm{div}[\mu\rho_0 e^{-\beta[\varphi(\vec{x}) - \psi(\vec{x})]}\,\mathrm{grad}\varphi(\vec{x})] - Q(\vec{x}) + R(\vec{x}) = 0 , \tag{19}$$

$$\Delta\psi(\vec{x}) = -(e^2/\epsilon\epsilon_0)\rho_0(e^{-\beta[\varphi(\vec{x}) - \psi(\vec{x})]} - e^{-\beta(\varphi - \psi)_0}) , \tag{20}$$

for the unknown functions $\varphi(\vec{x})$ and $\psi(\vec{x})$, where $(\varphi - \psi)_0$ is the difference of these functions in the undisturbed bulk.

Equations (19) and (20) cannot be solved as such as Q and R depend on the statistical impurity distributions and are thus random functions. The randomness itself has, however, no intrinsic consequences for the effect studied. As we are only interested in its qualitative features, we may assume for mathematical convenience a regular distribution, thereby retaining the local character of the wave functions. Moreover it is clear from symmetry reasons that all currents perpendicular to the c axis compensate. We may thus make the usual approximation of semiconductor transport and neglect fluctuations of the electric and electrochemical potentials perpendicular to the external current. Integrating Eqs. (19) and (20) over these directions we obtain

$$\frac{d}{dz}\,\mu\rho_0 e^{-\beta[\varphi(z) - \psi(z)]}\frac{d\varphi}{dz} - \bar{Q}(z) + \bar{R}(z) = 0 , \tag{21}$$

$$\frac{d^2\psi}{dz^2} = -\frac{e^2}{\epsilon\epsilon_0}\bar{\rho}_0\,(e^{-\beta[\varphi(z) - \psi(z)]} - e^{-\beta(\varphi - \psi)_0}) , \tag{22}$$

where we have introduced the averaged emission and recombination rates

$$\bar{Q}(z) = \frac{1}{F}\int_F dx\,dy\,Q(\vec{x})$$

and

$$\bar{R}(z) = \frac{1}{F}\int_F dx\,dy\,R(\vec{x}) . \tag{23}$$

Here F is some large surface perpendicular to the c axis. Equations (21) and (22) are coupled differential equations of one single variable and may in principle be solved numerically for any given $R(z)$ and $Q(z)$.

An analytical solution may be found if we assume that the range of all emitted carriers is the same and that recombination at the impurities is strictly local. This means that we approximate $R(z)$ and $Q(z)$ by

$$\begin{aligned} \bar{R}(z) &= \bar{R}\,\sum_i \delta(z - z_i) , \\ \bar{Q}(z) &= \bar{Q}\,\sum_i \delta(z - z_i - \Lambda_0) , \end{aligned} \tag{24}$$

as indicated in Fig. 3, where Λ_0 is the range of the emitted photoelectrons and z_i is the coordinate of the ith impurity along the c axis. There are now two distinct regions which we label A for the range over which the photoelectrons travel before being randomized, i.e., from each z_i to $z_i + \Lambda_0$ and B for the range from there to the next impurity. Inside these regions there is no generation or recombination and we have from (17) $j(z) = j = \mathrm{const}$ and from Eq. (18)

$$\frac{d\varphi}{dz} = \frac{j}{e\mu\rho_0}\,e^{\beta[\varphi(z) - \psi(z)]} . \tag{25}$$

Integrating Eq. (17) over the intervals $[z_i - \epsilon, z_i + \epsilon]$ and $[z_i + \Lambda_0 - \epsilon_1, z_i + \Lambda_0 + \epsilon]$ and taking the limit $\epsilon \to 0$ we obtain

$$j_B - j_A = e\bar{Q}$$

and

$$\bar{R} = \bar{Q} , \tag{26}$$

which is the condition for conservation of the particle number.

For all practical purposes we have to do with large gap materials so that ρ is very small and thus

$$d^2\psi/dz^2 \simeq 0 , \tag{27}$$

and we may take approximately $\psi(z) = \psi = \mathrm{const}$. This assumption corresponds to taking $\tau_r \to \infty$ in Eq. (11). It has been checked numerically and is found to be a good approximation for reasonable values of the parameters.

From the definition of the currents we see immediately that j_B is the external current while in region A we have the backflow $j_A = j_B - eQ$ within the local dipole. It should be emphasized that we are always treating a stationary case and that this dipole is therefore constant in time.

V. SHORT-CIRCUIT CASE

In the short-circuit case the boundary values of $\varphi(z)$ are equal at both ends of the specimen $\varphi(\pm\infty) = \varphi_0$ and from (27) we have $\psi(z) \simeq \psi = \text{const}$. φ being a continuous function of z and all impurities being equivalent in this case, we also have $\varphi = \varphi_0$ exactly twice between each two adjacent impurities along the c axis. In Fig. 4(a) this is shown schematically for the ith impurity with $\varphi(z_i - \eta_1) = \varphi(z_i + \eta_2) = \varphi_0$. It should be emphasized that this shape of φ though it has some apparent similarity to the band bending of the model discussed in Ref. 10 is an entirely different physical situation. In our case the bands, whose shape is given by $\psi(z)$ are flat according to Eq. (27).

Inverting Eq. (25) we obtain

$$\frac{dz}{d\varphi} = \frac{e\mu\rho_0}{j}\, e^{-\beta[\varphi(z)-\psi(z)]}, \tag{28}$$

which has the solution

$$\varphi(z) = \psi - \frac{1}{\beta}\ln\left| -\frac{j\beta z}{e\mu\rho_0} + e^{-\beta(\hat\varphi-\psi)}\right|, \tag{29}$$

$\hat\varphi$ being the function value at some arbitrarily chosen $z = 0$. As in Sec. IV we separate the range between the impurities into sections A and B, where $j_B = J$ is the external current and $j_A = J - eQ$. Therefore,

$$\varphi_A(z) = \psi - \frac{1}{\beta}\ln\left| -\frac{(J-eQ)\beta z}{e\mu\rho_0} + e^{-\beta(\hat\varphi_A-\psi)}\right|, \tag{30}$$

$$\varphi_B(z) = \psi - \frac{1}{\beta}\ln\left| -\frac{J\beta z}{e\mu\rho_0} + e^{-\beta(\hat\varphi_B-\psi)}\right|. \tag{31}$$

Continuity of φ requires

$$\varphi_A(z_i) = \varphi_B(z_i), \tag{32}$$

$$\varphi_A(z_i + \eta_2) = \varphi_B(z_i - \eta_1). \tag{33}$$

From Eqs. (30)–(32) we obtain

$$e^{-\beta(\hat\varphi_B-\psi)} = eQ\beta z_i/e\mu\rho_0 + e^{-\beta(\hat\varphi_A-\psi)}, \tag{34}$$

and inserting this into (33) gives

$$J = eQ\eta_2/(\eta_1+\eta_2). \tag{35}$$

From the above definition and from Fig. 4(a) we see immediately that $\eta_1 + \eta_2 = \frac{1}{2}\bar{c}$, where $\bar{c}$ is the mean distance between the impurities along the c axis and $\eta_2 = \frac{1}{2}\Lambda_0$. $\bar{Q}$ is according to (23) and (24) the average excitation efficiency at $z = z_i$. Introducing $\bar{a}$ and $\bar{b}$ as the mean impurity separations perpendicular to the c axis and Q_0 as the excitation efficiency per impurity we obtain

$$J_{sc} = eQ_0\rho_{\text{imp}}\Lambda_0, \tag{36}$$

where $\rho_{\text{imp}} = (\bar{a}\bar{b}\bar{c})^{-1}$ is the concentration of "active" impurities. We see thus that the external short-circuit current only depends on the photoexcitation efficiency and range of the active impurities. It does, however, not depend on the conductivity of the specimen. This result as well as the linear dependence on concentration of Eq. (36) is in agreement with experiment.[13]

There may be additional contributions to the external current due to an asymmetry of recombination and to asymmetric scattering. These effects depend on the configuration of the impurities and are not being discussed here.

VI. OPEN-END CASE

In the open-end case the external current vanishes. Outside the range of the direct motion of the photoelectrons we have thus $j_B = 0$ and from (19) $d\varphi/dz = 0$. For the regions A between impurity and target we have from Eq. (26) $j_A = e\bar{Q}$, and taking again $\psi(z) = \psi = \text{const}$ we have

$$\frac{d\varphi}{dz} = \frac{eQ}{\mu\rho_0}\, e^{\beta[\varphi(z)-\psi]}. \tag{37}$$

This situation is shown in Fig. 4(b). The potential difference $\Delta\varphi$ generated in stationary state at z_i becomes

$$\Delta\varphi = \int_{z_i}^{z_i+\Lambda_0} dz\, \frac{d\varphi}{dz}. \tag{38}$$

In Eq. (37) $(e\mu\rho_0)^{-1}\exp\{\beta[\varphi(z) - \psi]\}$ is the local resistivity which depends through $\varphi(z)$ on the particle density. Averaging this over the current carrying region we obtain the mean resistivity

$$\frac{1}{\sigma} = \frac{1}{e\mu\rho_0}\,\frac{1}{\Lambda_0}\int_{z_i}^{z_i+\Lambda_0} dz\, e^{\beta[\varphi(z)-\psi]}, \tag{39}$$

which is the reciprocal of the normal bulk photo-

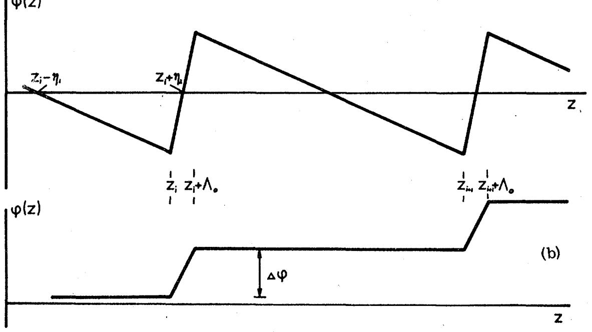

FIG. 4. Electrochemical potential |π between two impurities along the c axis (a) in the short-circuit case and (b) for open ends.

conductivity. Inserting (39) into (38) we obtain

$$\Delta\varphi = e\overline{Q}\Lambda_0/\sigma . \tag{40}$$

The saturation field $E_s = \Delta\varphi/\overline{c}$ is then

$$E_s = e\overline{Q}\Lambda_0/\overline{c}\sigma , \tag{41}$$

and with (36) we find finally

$$E_s = J_{sc}/\sigma . \tag{42}$$

Saturation field and short-circuit current are thus connected by a relation of the type of Ohm's law where the proportionality constant is the photoconductivity. This result is confirmed by experiment.

VII. SUMMARY

The problems in understanding the transport processes leading to the bulk photovoltaic effect are twofold: (i) photoelectrons must somehow acquire a spontaneous momentum, and (ii) the electrons must continue their motion in the preferred direction over macroscopic distances in order to generate a direct electric current.

The requirement for momentum imbalance violates time-reversal symmetry. This was discussed in Sec. II and it was shown that impurity or defect states allow for the BPVE while it is impossible in bands of pure Bloch states. With respect to the second point mentioned above the problem lies in explaining the fact that the excited electron separates from the impurity and keeps on moving in the preferred direction in spite of scattering and even against a macroscopic field.

Using a diffusion formalism we showed in Secs. IV–VI that there exists a stationary state in which only part of the emitted electrons flow back to the impurities while the rest experiences a driving force along the *c* axis from the gradient of the electrochemical potential.

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