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Photogalvanic effect in a crystal with polar axis

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Photoelectric emf mechanisms governed only by the symmetry of the crystal—by the presence of a polar axis—are proposed. They are based on the asymmetry of the electronic processes—their non-invariance to spatial reflections.

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INTRODUCTION

The photoelectric-emf mechanisms connected with the inhomogeneity of crystals and with the non-uniformity of their illumination are well known.[1] There are, however, experimental data indicating that emf is produced in homogeneous ferroelectrics that are uniformly illuminated.[2,3] The existence of photo-induced currents is due in this case to the crystal symmetry—the presence of a polar axis in the crystal[2]; this effect does not exist in the para-phase. The currents observed in short-circuited samples are small ($j_{ph} \approx 10^{-8}$–10^{-9} A/cm^2 at $J \sim 1$ W/cm^2), but when isolated crystals are illuminated charge transfer gives rise to blocking fields $E_0 \sim 10^3$–10^5 V/cm.

Consider the expansion of the constant electric current in power of the field of the light wave $\vec{\mathbf{E}}(\omega)$ and the constant field $\mathbf{E}$:

$$j_i = \sigma_{ik}E_k + \beta_{ikl}E_kE_l + \gamma_{iklm}E_kE_lE_m + \ldots .$$

Here σ_{ik} is the intrinsic conductivity of the crystal, γ_{iklm} is the photoconductivity, and β_{ikl} describes the effect considered by us, namely a current in the absence of a constant field. If the crystal has a polar axis, then we can construct the tensor β_{ikl}:

$$\beta_{ikl} = \alpha c_i\delta_{kl} + \beta c_ic_kc_l + \gamma(c_i\delta_{ik} + c_k\delta_{il}), \quad (1)$$

and the unit vector e specifies the polar direction of the crystal. The quantities $\alpha(\omega)$, $\beta(\omega)$, and $\gamma(\omega)$ should be determined by the microscopic approach. Expression (1) for β_{ikl} is not the most general one, since it does not take into account the singularities of the crystal symmetry. Photocurrent is possible if the crystal symmetry allows the existence of the tensor β_{ikl}.

We propose an elementary theory of the effect. This theory is based on the asymmetry of the elementary electronic processes—their noninvariance to spatial reflections. It is assumed that the dielectric has in its forbidden band an impurity level to depth Δ, from which the photoexcited electrons stem. The electrons in the conduction band will be described by the kinetic equation for the distribution function f_k:

$$\frac{\partial f_k}{\partial t} = I_k^i - I_k^r + I_k^{imp} + I_k^{ph}, \quad (2)$$

where $I_m^{ex}(f_k)$ and $I_k^r(f_k)$ are respectively the electron excitation and recombination rates, while $I_k^{imp}(f_k)$ and $I_k^{ph}(f_k)$ are the integrals of the collisions with the impurities and the phonons.

The idea of the effect is the following: Assume that the

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right-hand side of (2) contains an asymmetrical term $I_{\mathbf{k}}^{as}(f_{\mathbf{k}})$ having the property

$$I_{\mathbf{k}}^{as}(f_{\mathbf{k}}^{as})=-I_{-\mathbf{k}}^{as}(f_{\mathbf{k}}^{as}); \quad f_{\mathbf{k}}^{as}=f_{-\mathbf{k}}^{as}. \tag{3}$$

The stationary solution of the kinetic equation cannot be purely symmetrical in this case, but must contain an asymmetrical part

$$f_{\mathbf{k}}^{as}=-f_{-\mathbf{k}}^{as},$$

which leads, in accordance with the general formula

$$\mathbf{j}=\frac{e}{\hbar}\int\frac{\partial\varepsilon_{\mathbf{k}}}{\partial\mathbf{k}}f_{\mathbf{k}}\,d\mathbf{k}=\frac{e}{\hbar}\int\frac{\partial\varepsilon_{\mathbf{k}}}{\partial\mathbf{k}}f_{\mathbf{k}}^{as}\,d\mathbf{k} \tag{4}$$

to the appearnce of a current. We emphasize that we are dealing here with a nonequilibrium situation: the asymmetric collision term $I_{\mathbf{k}}^{as}$ and the current $\mathbf{j}_{ph}$ always vanish on the equilibrium electron distribution functions. We consider the origin and structure of the asymmetric probabilities of the scattering (Sec. 1) as well as of the probabilities of the ionization and recombination (Sec. 2).

Equation (2) contains four characteristic times: the time γ^{-1} of the electron recombination on the impurity, the time Γ_{imp}^{-1} between the collisions between the impurities, the time Γ_t^{-1} of relaxation to the Boltzmann distribution function, and the time Γ_i^{-1} of momentum isotropization. We assume that

$$\Gamma_t \gg \Gamma_i, \quad \Gamma_{imp} \gg \gamma. \tag{5}$$

The isotropization and thermalization will be assumed to be connected with the phonons, $I_{\mathbf{k}}^{ph}=I_{\mathbf{k}}^{i}+I_{\mathbf{k}}^{is}$. We also fix the explicit form of $I_{\mathbf{k}}^{is}$

$$I_{\mathbf{k}}^{is}=-\Gamma_i(f_{\mathbf{k}}-\bar{f}_{\mathbf{k}}), \tag{6}$$

where the bar denotes averaging over the constant-energy surface.

Using (5) and (6), we readily obtain the stationary solutions of (2)

$$f_{\mathbf{k}}=f_{\mathbf{k}}^{0}+f_{\mathbf{k}}^{1}+f_{\mathbf{k}}^{2}+\ldots.$$

Here $f_{\mathbf{k}}^{0}$ is the Boltzmann distribution function normalized to the total electron concentration in the conduction band,[1)]

$$\begin{aligned} f_{\mathbf{k}}^{1}&=\Gamma_i^{-1}[I_{\mathbf{k}}^{t}(f_{\mathbf{k}}^{0})-I_{\mathbf{k}}^{\gamma}(f_{\mathbf{k}}^{0})+I_{\mathbf{k}}^{imp}(f_{\mathbf{k}}^{0})],\\ f_{\mathbf{k}}^{2}&=\Gamma_i^{-1}[I_{\mathbf{k}}^{t}(f_{\mathbf{k}}^{1})-I_{\mathbf{k}}^{\gamma}(f_{\mathbf{k}}^{1})+I_{\mathbf{k}}^{imp}(f_{\mathbf{k}}^{1})+I_{\mathbf{k}}^{t}(f_{\mathbf{k}}^{1})]. \end{aligned} \tag{7}$$

The use of (4) and (7) leads to simple estimates of the effect if the concrete model of $I_{\mathbf{k}}^{as}$ is specified.

1. ASYMMETRY OF SCATTERING

We consider elastic scattering of electrons by randomly disposed impurities. This process corresponds to the usual collision term in the kinetic equation

$$I_{\mathbf{k}}^{imp}=\int(W_{\mathbf{kk}'}f_{\mathbf{k}'}-W_{\mathbf{k}'\mathbf{k}}f_{\mathbf{k}})\delta(\varepsilon_{\mathbf{k}}-\varepsilon_{\mathbf{k}'})\,d\mathbf{k}' \tag{8}$$

where $W_{\mathbf{kk}'}$ is the probability of electron scattering from a state with momentum $\mathbf{k}'$ into a state $\mathbf{k}$. If $w_{\mathbf{kk}'}$ is the transition probability for one center, then $W_{\mathbf{kk}'}=Cw_{\mathbf{kk}'}$, where C is the impurity concentration.

The only general symmetry relation for $W_{\mathbf{kk}'}$ follows from the invariance of the equations of motion to time reversal[4] (the reciprocity theorem)

$$W_{\mathbf{kk}'}=W_{-\mathbf{k}',-\mathbf{k}}. \tag{9}$$

Besides (9), it is frequently assumed that the relation $W_{\mathbf{kk}'}=W_{\mathbf{k}'\mathbf{k}}$ (the detailed balancing principle) is satisfied. It is well known, however (see e.g.,[4,5]) that this property holds only for symmetric potentials $U(\mathbf{r})=U(-\mathbf{r})$. The absence of detailed balancing is of fundamental importance to us. It must be noted that we assume the randomly disposed centers to have identical orientations. This is precisely of the presence of the polar axis manifests itself in the crystal. If, for example, the noncentrality of the impurity is due to its dipole moment, then all dipoles must have the same orientation.

Using (9), we represent $W_{\mathbf{kk}'}$ in the form

$$W_{\mathbf{kk}'}=W_{\mathbf{kk}'}^{s}+W_{\mathbf{kk}'}^{as}, \tag{10}$$

where

$$W_{\mathbf{kk}'}^{s}=W_{\mathbf{k}'\mathbf{k}}^{s}=W_{-\mathbf{k},-\mathbf{k}'}^{s}, \quad W_{\mathbf{kk}'}^{as}=-W_{\mathbf{k}'\mathbf{k}}^{as}=-W_{-\mathbf{k},-\mathbf{k}'}^{as}.$$

The collision term is then written in the form

$$\begin{aligned} I_{\mathbf{k}}^{imp}&=\int W_{\mathbf{kk}'}^{s}(f_{\mathbf{k}'}-f_{\mathbf{k}})\delta(\varepsilon_{\mathbf{k}}-\varepsilon_{\mathbf{k}'})\,d\mathbf{k}'\\ &+\int W_{\mathbf{kk}'}^{as}(f_{\mathbf{k}'}+f_{\mathbf{k}})\delta(\varepsilon_{\mathbf{k}}-\varepsilon_{\mathbf{k}'})\,d\mathbf{k}'. \end{aligned} \tag{11}$$

As seen from (10) and (11),

$$I_{\mathbf{k}}^{as}=\int W_{\mathbf{kk}'}^{as}(f_{\mathbf{k}}+f_{\mathbf{k}'})\delta(\varepsilon_{\mathbf{k}}-\varepsilon_{\mathbf{k}'})\,d\mathbf{k}' \tag{12}$$

does indeed have the property (3).

We consider now the question of the vanishing of $I_{\mathbf{k}}^{as}$ on the equilibrium distribution function. The sufficient condition for this is, obviously,

$$\int W_{\mathbf{kk}'}^{as}\delta(\varepsilon_{\mathbf{k}}-\varepsilon_{\mathbf{k}'})\,d\mathbf{k}'=0. \tag{13}$$

It is shown in the Appendix that this condition is always satisfied for elastic scattering. Thus, $I_{\mathbf{k}}^{as}=0$ on any function of the energy. On the other hand, if external sources provide an increment $\delta f_{\mathbf{k}}$ that is not a function of $\varepsilon_{\mathbf{k}}$, then this increment must have an asymmetric part, i.e., a current is produced.

Let us consider a concrete model. Let the scattering center have a short-range symmetric potential with a scattering length a and an asymmetric dipole potential[2)]

$$U^{as}=e(\mathbf{dr})/\varepsilon_0 r^3, \tag{14}$$

where ε_0 is the permittivity. Assuming both potentials to be small, we use perturbation theory. To determine $W_{\mathbf{kk}'}^{as}$ we must calculate the scattering amplitude up to second order in the potential (see[4]). The contribution to $W_{\mathbf{kk}'}^{as}$ comes from the product of the amplitude in first

order of perturbation theory by the pole contribution to the amplitude in second order. In the free electron approximation $\varepsilon_{\mathbf{k}}=k^2\hbar^2/2m$ and

$$W_{\mathbf{kk}'}^{as}=\frac{4e\hbar a^2C}{\varepsilon_0 mk}\frac{\mathbf{kk}'}{|\mathbf{k}-\mathbf{k}'|^2}(\mathbf{d},\mathbf{k}-\mathbf{k}'). \tag{15}$$

It is easy to verify that $W_{\mathbf{kk}'}^{as}$ satisfies relation (13). To calculate the symmetric part $W_{\mathbf{kk}'}^{s}$ it is necessary to take into account in explicit form the screening of the dipole potential at large distances. In addition, it is necessary to take into account the scattering by the symmetric traps from which the electrons are photoexcited. We assume that the total $(I_{\mathbf{k}}^{imp})^s$ is included in (6).

We specify also the ionization and recombination model. Let the electrons be excited from symmetric centers having only S states. Then the number of electrons excited with momentum $\mathbf{k}$ per unit time and unit volume can be expressed in the form

$$I_{\mathbf{k}}{}^{i}=I_{-\mathbf{k}}{}^{i}=\frac{3\varkappa J}{4\pi k^2\hbar\omega}\frac{(\mathbf{ke})^2}{k^2}\delta(k-k_0). \tag{16}$$

Here $\varkappa$ is the absorption coefficient, $\mathbf{e}$ is the polarization vector, and k_0 is defined by the conservation law: $\hbar\omega=\Delta+\varepsilon_{k_0}$. The anisotropy of the excitation is thus due in our case to the polarization of the light. The recombination term, which contains the emitted photons averaged over the polarizations and momenta, makes therefore no contribution to $f_{\mathbf{k}}^{as}$. Let us finally determine the current. As seen from (7), $f_{\mathbf{k}}^{as}$ appears in the second-order perturbation-theory solution of the kinetic equation:

$$f_{\mathbf{k}}{}^{as}=\Gamma_i^{-2}\int W_{\mathbf{kk}'}^{as}I_{\mathbf{k}'}{}^{i}\delta(\varepsilon_{\mathbf{k}}-\varepsilon_{\mathbf{k}'})d\mathbf{k}'$$
$$=\frac{\varkappa J}{\hbar\omega}\frac{e\hbar a^2Cd}{\varepsilon_0 mk\Gamma_i^2}\left[(\mathbf{ce})(\mathbf{ke})-\frac{(\mathbf{ck})(\mathbf{ek})^2}{k^2}\right]\delta(\varepsilon_{\mathbf{k}}-\varepsilon_{k_0}). \tag{17}$$

Substituting this in (4) we obtain (see also (1)):

$$\mathbf{j}_{ph}=\frac{4\pi}{15}(k_0a)^2\frac{\varkappa J}{\hbar\omega}\frac{e^2d}{\varepsilon_0\Gamma_i^2 m}(\mathbf{c}-3\mathbf{e}(\mathbf{ce})). \tag{18}$$

We point out that in our model the direction of the current depends essentially on the polarization of the light. Thus, the currents have opposite signs in the cases $\mathbf{e}\perp\mathbf{c}$ and $\mathbf{e}\parallel\mathbf{c}$. The average of j_{ph} over the polarization and direction of the light is zero.

We note the anisotropy of the excitation (as well as of the recombination) can be due not only to the polarization of the light, but also to the polar axis. In fact, if the localized electrons are in a P state with quantization axis along the polar axis, then the probabilities of the ionization and recombination of the electrons remain anisotropic also after the averaging over the polarizations and directions of the light. The anisotropy of the recombination leads to an additional contribution to the current. It can be shown that this contribution manifests itself in the appearance of a characteristic factor of the type $(1-k_T^2/k_0^2)$ in Eq. (18) ($k_T=(mT)^{1/2}/\hbar$ is the average electron momentum in thermal equilibrium).

Despite the idealized character of our model, expression (18) can be regarded as an estimate of the current based on the scattering mechanism. Putting $=1\ \text{cm}^{-1}$, $d=0.1\,ea$, $a=10^{-8}$ cm, $\Gamma_i=10^{13}\ \text{sec}^{-1}$, $k_0a=0.1$, $\varkappa\hbar\omega=5\times10^{-12}$ erg, $C=10^{18}\ \text{cm}^{-3}$, and $\varepsilon_0=10$, we obtain

$$j_{ph}[\text{A/cm}^2]=10^{-11}J[\text{W/cm}^2].$$

Let us estimate also the blocking field E_0, determined from the vanishing of the total current

$$\mathbf{j}=\mathbf{j}_{ph}-\sigma_{ph}\mathbf{E},$$

where σ_{ph} is the photoconductivity. Assuming $\sigma_{ph}[\Omega^{-1}\,\text{cm}^{-1}]=10^{-12}J[\text{W/cm}^2]$ (these values correspond to the experimental conditions of[21]), we get

$$E_0=10^2\ \text{V/cm},$$

which is independent of the intensity of the light.

2. ASYMMETRY OF EXCITATION AND RECOMBINATION

In our analysis of the asymmetry of $I_{\mathbf{k}}^{i}$ and $I_{\mathbf{k}}^{r}$ we confine ourselves to pure radiative processes and retain terms of lowest order in the light intensity

$$I_{\mathbf{k}}{}^{i}=C\sum_{\alpha}\int w_{\alpha}{}^{i}(\mathbf{k},\mathbf{q})n_{\alpha}(\mathbf{q})d^3q,$$
$$I_{\mathbf{k}}{}^{r}=(C_0-C)\sum_{\alpha}\int w_{\alpha}{}^{r}(\mathbf{k},\mathbf{q})f_{\mathbf{k}}d^3\mathbf{q}. \tag{19}$$

Here $n_\alpha(\mathbf{q})$ is the number of photons with polarization α and momentum q, $w_\alpha^{i,r}(\mathbf{k},\mathbf{q})$ are the probabilities of ionization and recombination on the impurity level, C is the number of electrons on the impurities, and C_0 is the total number of impurities.

For impurity—band transition we can use the dipole approximation, and the quantities $w_\alpha^{i,r}(\mathbf{k},q)$ do not depend explicitly on the photon momentum[6]:

$$w_{\alpha}^{i,r}(\mathbf{k})=\frac{\omega}{2\pi}|\langle\mathbf{k}\pm|\mathbf{e}_\alpha\mathbf{D}|0\rangle|^2\delta(\hbar\omega-\Delta-\varepsilon_{\mathbf{k}}). \tag{20}$$

Here D is the dipole-moment operator, $\mathbf{e}_\alpha$ is the polarization vector, ψ_0 is the wave function of the electron on the impurity, and $\psi_{\mathbf{k}}^{\pm}$ are the wave functions of the free electrons and contain diverging and converging waves.

The probabilities $w_\alpha^{i,r}(k)$ are connected by the relation

$$w_{\alpha}{}^{i}(\mathbf{k})=w_{\alpha}{}^{r}(-\mathbf{k})\neq w_{\alpha}{}^{i}(-\mathbf{k}), \tag{21}$$

which follows from the invariance to time reversal. Relations (20) and (21) show that in the absence of a symmetry center the quantities $I_{\mathbf{k}}^{i,r}$ contain asymmetric parts

$$(I_{\mathbf{k}}^{i,r})^{as}=-(I_{-\mathbf{k}}^{i,r})^{as}. \tag{22}$$

We call attention to the following circumstance: it follows from (19) and (21) that at equilibrium $(I_{\mathbf{k}}^{i,r})^{as}$ do not vanish and make contributions of like sign to the complete collision integral. The reason is that the kinetic equation contains additional terms of the same order as the contribution from the ionization and recombination processes. It is shown in the Appendix that in the presence of absorbing centers, i.e., recombination

processes, the asymmetric part of the scattering probability satisfies in lieu of (13) the relation

$$(I_{\mathbf{k}}^{\mathrm{imp}})^{as}=\int (f_{\mathbf{k}}+f_{\mathbf{k}'})W_{\mathbf{k}\mathbf{k}'}^{as}\delta(\varepsilon_{\mathbf{k}}-\varepsilon_{\mathbf{k}'})d\mathbf{k}'=2(I_{\mathbf{k}}^{r})^{as}. \tag{23}$$

This formula is valid if $f_{\mathbf{k}}$ is a function of the energy. It is easy to verify that $(I_{\mathbf{k}}^{i}-I_{\mathbf{k}}^{r}+I_{\mathbf{k}}^{\mathrm{imp}})^{as}$ vanishes at equilibrium (in our case, on the Boltzmann functions for the electrons and photons).

Taking (7) and (23) into account we write down the asymmetric correction to the distribution function in the form

$$f_{\mathbf{k}}^{as}=\Gamma_{f}^{-1}[I_{\mathbf{k}}^{i}(f_{\mathbf{k}}^{0})+I_{\mathbf{k}}^{r}(f_{\mathbf{k}}^{0})]^{as}, \tag{24}$$

where $f_{\mathbf{k}}^{0}$ is the Boltzmann distribution function normalized by the condition $\int f_{\mathbf{k}}^{0}d\mathbf{k}=C_0-C$. In contrast to (17), a current appears already in the first-order approximation in γ/Γ_f.

We assume now that the symmetric part of the potential, which produces the localized state, is short-range $kr_0\ll 1$, where r_0 is the effective radius of the potential. We again assume a dipole asymmetric part U^{as}. We note further that if wave functions $\psi_{\mathbf{k}}^{\pm}$ of the continuous spectrum are taken to be functions $\psi_{\mathbf{k}}^{\pm s}$ that take only the symmetric potential into account, then the relation $\psi_{\mathbf{k}}^{\pm s}=(\psi_{-\mathbf{k}}^{\pm s})^{*}$ leads to $I_{\mathbf{k}}^{i,r}=I_{-\mathbf{k}}^{i,r}$. It is therefore necessary to retain in $\psi_{\mathbf{k}}^{\pm}$ the correction due to the asymmetric potential U^{as}.[2,7] Assuming this potential to be small enough,[3)] we get[4]

$$\delta\psi_{\mathbf{k}}^{\pm as}(\mathbf{r})=\int\frac{\langle s,\mathbf{k}'\pm|U^{as}|s,\mathbf{k}\pm\rangle}{\varepsilon_{\mathbf{k}}-\varepsilon_{\mathbf{k}'}\pm i\varepsilon}\psi_{\mathbf{k}'}^{\pm s}(\mathbf{r})d\mathbf{k}'. \tag{25}$$

We recognize now that to calculate the matrix element $\langle\mathbf{k}\pm|\mathbf{D}|0\rangle$ we need know $\psi_{\mathbf{k}}^{\pm}(\mathbf{r})$ only at $r\lesssim r_0\ll k^{-1}$. In this region we can regard $\psi_{\mathbf{k}}^{\pm s}$ as independent of $\mathbf{k}'$:

$$\psi_{\mathbf{k}'}^{+s}(\mathbf{r})=(\psi_{\mathbf{k}'}^{-s}(\mathbf{r}))^{*}\approx\chi(\mathbf{r}).$$

The opposite limiting case is realized in the calculation of $\langle s,\mathbf{k}'\pm|U^{as}|s,\mathbf{k}\pm\rangle$, namely, since U^{as} is long-range, the main contribution in the integration is made by the region $r_0\ll r\lesssim k^{-1}$, so that $\psi_{\mathbf{k}}^{\pm s}(\mathbf{r})$ can be regarded as independent of the symmetric potential. In the free-electron approximation we have

$$\langle s,\mathbf{k}'\pm|U^{as}|s,\mathbf{k}\pm\rangle=\frac{ie}{2\pi^2}\frac{(\mathbf{d},\mathbf{k}-\mathbf{k}')}{|\mathbf{k}-\mathbf{k}'|^2}. \tag{26}$$

Finally, calculating $\delta\psi_{\mathbf{k}}^{as}$, we obtain

$$\delta\psi_{\mathbf{k}}^{+as}=-\delta\psi_{\mathbf{k}}^{-as}=\frac{em(\mathbf{dk})}{\pi k\hbar^2}\chi. \tag{27}$$

We have retained only the pole contribution in (25), since the contribution from the principal value has in our approximation the same symmetry as $\psi_{\mathbf{k}}^{s}$.

The subsequent calculations depend on the quantum numbers of the impurity levels. If the electrons on the impurities are in P states with quantization axis along the crystal axis, then

$$(I_{\mathbf{k}}^{ii,r})^{as}=\pm\frac{2em(\mathbf{dk})}{\pi k\hbar^2}(I_{\mathbf{k}}^{i,r})^{s}. \tag{28}$$

With the aid of (24) and (28) we obtain an expression for the current

$$j=\frac{2}{3\pi}\left(\frac{e^2k_0}{\hbar\omega}\right)\left(\frac{\varkappa Jd}{\hbar\Gamma_i}\right)\left(1-\left(\frac{8}{\pi}\right)^{1/3}\frac{k_T}{k_0}\right)\mathbf{e}. \tag{29}$$

Here $\varkappa\propto(\mathbf{c}\cdot\mathbf{e})^2$; this relation corresponds to vanishing of the coefficients α and γ in (1).

The reversal of the sign of j_{ph} at small k_0 has a simple meaning. The electron has a momentum k_0 as it enters the conduction band and the average thermal momentum k_T on departure. Therefore ionization or recombination prevails, depending on the value of k_T/k_0. It is appropriate to note that the reversal of the sign of the current as a function of the frequency, polarization, or radiation direction (see (18) and (29)) is not a property peculiar to the considered impurity models and scattering mechanisms. This property stems only from the fact that in the model assumed by us for the ionization and recombination (19) the current is linear in the light intensity and vanishes on the equilibrium distribution function of the photons.[5)]

To conclude this section, we present estimates for the current j_{ph} and for the blocking field E_0. For the previously assumed crystal parameters we have

$$j_{ph}[\mathrm{A/cm^2}]\approx 10^{-6}J[\mathrm{W/cm^2}],$$

$$E_0\approx 10^4\ \mathrm{V/cm},$$

i.e., in reasonable agreement with experiment.[2,3]

CONCLUSION

1. Calculation of the effect in a real crystal must of course take into account the actual singularities of the impurity centers, the band structure, the presence of many excitation and recombination channels, etc. This problem is outside the scope of this paper and should apparently be solved for actual types of crystals. It can, however, be expected that the mechanisms proposed by us for the effect are realized also in more complicated situations.

2. We note finally that the effect considered can exist also in impurity-free crystals, since the asymmetry of the unit-cell potential of a pyroelectric leads to asymmetry of the electron-phonon interaction.[7]

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APPENDIX

We introduce the quantity $Z_{\mathbf{k}}$, which has the meaning of the probability of the departure of the electron from the state $\mathbf{k}$. The probability $Z_{\mathbf{k}}$ consists of the total scattering probability and the probability of capture (recombination) by the scattering center. By virtue of the optical theorem[4]

$$Z_{\mathbf{k}}=\int w_{\mathbf{k}'\mathbf{k}}\delta(\varepsilon_{\mathbf{k}}-\varepsilon_{\mathbf{k}'})d\mathbf{k}'+w_{\mathbf{k}}^{r}=4\pi\,\mathrm{Im}\,f_{\mathbf{k}\mathbf{k}}, \tag{A.1}$$

where $f_{\mathbf{k}\mathbf{k}}$ is the forward-scattering amplitude. Accord-

ing to the reciprocity theorem, however, $f_{kk}=f_{-k,-k}$, so that $Z_k=Z_{-k}$ and consequently

$$\int w_{k'k}^{as}\delta(\varepsilon_k-\varepsilon_{k'})dk'+w_k^{p,as}=0. \qquad (A.2)$$

If the scattering potential has no bound states, $I_k^r=0$, then (A.2) leads to (13). But if the center has an energy level, then radiative capture of an electron by the level is possible with a probability w_k^r. In this case (A.2) leads to relation (23).

For the model considered in the text (Sec. 2), the additional contribution to the collision integral is due to the quantum-electrodynamic process of virtual emission of a photon by the electron and the transition of the electron to the impurity level, the subsequent absorption of the photon, and the return of the electron to the band.

[1)]The latter is determined from the condition.

$$\int (U_k^i-I_k^r)dk=0$$

[2)]The macroscopic field produced by polarized impurities has no bearing on our problem. It is determined by the boundary conditions and can be set equal to zero.

[3)]We note that the symmetric potential (unlike U^{as}) cannot be regarded as small, since it has a bound state.

[4)]We assume that the amplitude of scattering by a symmetric potential is of the order of r_0.

[5)]The reversal of the sign of the current as a function of the frequency and of the polarization of the light were observed in experiments.[3]

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Magnetic breakdown and thermoelectric power in niobium

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We measured the transverse magnetoresistance and thermoelectric power of a niobium sample with orientation [001] in fields up to 150 kOe. A large thermoelectric-power signal and its oscillations were observed at **H** ∥ [110]. Coherent magnetic breakdown in the region of the conical point contacts located on the ΓP symmetry lines, is invoked to explain the results.

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Experimental investigations of the influence of magnetic breakdown on the thermoelectric power of a number of simple metals yielded results that were so highly promising,[1–4] that it was proposed in[2] to use the thermoelectric power to study metals whose Fermi-metal topology impedes the onset of magnetic-breakdown resistance oscillations. This is precisely the situation in niobium, where the magnetic breakdown leads to a transition from open to closed trajectories,[5,6] and according to[7] this transition should not be accompanied by resistance oscillations.

We report here results of an investigation of the thermoelectric power of niobium in strong magnetic fields.

EXPERIMENT

The thermoelectric power and the magnetoresistance were measured on a niobium sample of orientation [001] with a resistance ratio $\rho_{300\,K}/\rho_{res}\approx 3000$. The mounting of the sample is shown in Fig. 1. Copper current leads were spark-welded through small nickel bushings. The potential leads of an alloy 70% Pb + 30% Sn, were spot-welded. The heater, with resistance ~20 Ω was bifilarly wound on a form and fastened with BF-2 adhesive, after which it was slipped over the "hot" end of the sample. To monitor the temperature gradient, a differential Cu–(Au + 0.07% Fe) thermocouple[8] was glued to the sample.

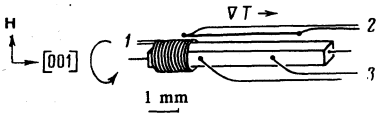

FIG. 1. Mounting of the sample for the measurement of the thermoelectric power and the magnetoresistance: 1—heater, 2—differential thermocouple, 3—potential leads.

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