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Theory of the bulk photovoltaic effect in pure crystals

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A theory is presented for the intrinisic anomalous bulk photovoltaic effect observed in noncentrosymmetric crystals, e.g., $BaTiO_3$. An exact formula is derived for the calculation of the short-circuit photovoltaic current in a pure crystal in terms of its Bloch states and energy bands. Unlike a conventional field or diffusion current, the photovoltaic current is essentially determined by the change of wave functions upon photoexcitation of an electron from the valence to the conduction band. Our theory also reveals that the bulk photovoltaic effect can occur even in pure nonpyroelectric piezoelectric crystals, e.g., Te and GaP, which have no polar axis and therefore no *a priori* direction for the photovoltaic current.

I. INTRODUCTION

Homogeneous illumination of pyroelectric single crystals, e.g., $LiNbO_3$ (Refs. 1–3) or $BaTiO_3$,[4] yield steady-state short-circuit photovoltaic currents (SCPVC) with density $\vec{j}$, although there is no macroscopic electric field or concentration gradient present. This phenomenon is called the bulk photovoltaic effect (BPVE). Usually, experimental results for the SCPVC are presented in the following form[1,3,4]

$$j=\kappa(\omega)\alpha(\omega)I_0 \text{ or } j=e\alpha(\omega)(I_0/\hbar\omega)s(\omega)\,, \tag{1}$$

where ω denotes the frequency, I_0 is the intensity of the radiation, and $\alpha(\omega)$ denotes the absorption coefficient of the crystal. In contrast to naive arguments, Glass's photovoltaic coefficient $\kappa(\omega)$, as well as the anisotropy distance $s(\omega)$, still depends on the frequency as well as on the polarization of the radiation. The direction of $\vec{j}$ is assumed to be parallel or antiparallel to the direction of the spontaneous polarization of the pyroelectric. However, it has been overlooked in the literature that this statement is only correct if the polarization vector $\vec{e}$ of the radiation is parallel to one of the crystal axes.

In order to stress the tensorial nature of the $\vec{j}-\vec{e}$ relationship, one should prefer instead of (1) the following form:

$$j_\nu=P_{\nu\mu\lambda}I_0e_\mu e_\lambda+D_{\nu\sigma\mu\lambda}I_0\hat{q}_\sigma e_\mu e_\lambda\,, \tag{2}$$

which is correct up to second order in the radiation electric field and up to first order in the photon momentum along unit vector $\hat{q}$. P and D denote the third-rank photovoltaic tensor[5-11] and the fourth-rank photondrag tensor,[10,11] respectively. In this article, subscripts $\nu\sigma\mu\lambda$ refer to Cartesian components. Usually, the photondrag term, which depends explicitly on the propagation direction of the radiation, is neglected when discussing the BPVE in pyroelectrics. However, it is well known[10,11] that photondrag effects may not be negligible.

It is the purpose of this paper to give an explicit representation of the photovoltaic tensor P for a pure noncentrosymmetric crystal whose electronic states are given by a set of Bloch states. In contrast to the results of other authors,[6-9,12-14] we conclude from our theory that a pure crystal can definitely exhibit a BPVE even though impurities or electron-phonon interactions are not considered. These results are supported by experimental data obtained for $LiNbO_3$ (Ref. 3) and $BaTiO_3$.[4] Furthermore, our theory reveals that the BPVE can occur even in nonpyroelectric piezoelectrics, as is observed, e.g., in Te (Ref. 10) or GaP.[11] These crystals are noncentrosymmetric, but they have no unique polar axis.

II. CALCULATION OF THE PHOTOVOLTAIC RESPONSE TENSOR

Our calculation of the SCPVC is based on a quadratic response theory which has been worked out for the BPVE by the present authors[5] and which was derived independently by Gulbis.[15] For a pure crystal, the general one-electron states $|l\rangle$, $|m\rangle$, $|n\rangle$ in formula (25) of Ref. 5 are given by Bloch states $|\vec{k},l\rangle$, etc. Here l denotes the band index and $\vec{k}$ denotes the wave vector which is confined to the first Brillouin zone. The required momentum matrix elements are diagonal with respect to $\vec{k}$,

$$\langle\vec{k}',n'|\vec{p}|\vec{k},n\rangle=\langle\vec{k},n'|\vec{p}|\vec{k},n\rangle\delta_{\vec{k},\vec{k}'}\,, \tag{3}$$

and the following symmetry relations hold:

$$\begin{aligned}&\langle\vec{k},n'|\vec{p}|\vec{k},n\rangle^*=-\langle-\vec{k},n'|\vec{p}|-\vec{k},n\rangle\,,\\&E_n(-\vec{k})=E_n(\vec{k})\,.\end{aligned} \tag{4}$$

These are a direct consequence of the reversibility of the solutions of the Schrödinger equation with respect to time[16,17] if $[H,K]=0$, irrespective of crystal symmetry. H denotes the Hamiltonian of electrons in the periodic crystal potential and K is the time-reversing operator. (Spin effects are not considered.)

$$K\Psi_{n,\vec{k}}(\vec{r})=\psi^*_{n,\vec{k}}(\vec{r})=\psi_{n,-\vec{k}}(\vec{r})\,. \tag{5}$$

Inserting (3) and (4) in (25) of Ref. 5 and replacing the sum over wave vector and spin by an integral according to

$$\sum_{\vec{k},s}\cdots=2\frac{V}{(2\pi)^3}\int d^3k\cdots\,, \tag{6}$$

we obtain the following relation for the SCPVC density:

$$\vec{j}=I_0\frac{|e|^3}{4\pi^3m_0^3\epsilon_0c\eta\omega^2}\,\mathrm{Re}\sum_{\Omega=\pm\omega}\sum_{l,m,n}\int_{\text{first BZ}}d^3k(f_l-f_n)\frac{\langle n,\vec{k}|\vec{e}\cdot\vec{p}|l,\vec{k}\rangle\langle l,\vec{k}|\vec{e}\cdot\vec{p}|m,\vec{k}\rangle\langle m,\vec{k}|\vec{p}|n,\vec{k}\rangle}{(E_n-E_m-i\delta)(E_n-E_l+\hbar\Omega-i\delta)}\,. \tag{7}$$

$E_n\equiv E_n(\vec{k})$ and $f_n\equiv f(E_n(\vec{k}))$ are, respectively, abreviations for the band energy and Fermi function, η denotes the index of refraction, m_0 is the free-electron mass, and δ denotes a positive infinitesimal quantity. By using (6), we have already performed the thermodynamic limit. Because there are no contributions to (7) from terms $l=n$ and $m=n$ we additionally may restrict the m summation to terms $m\neq n$.

Our analysis of (7) proceeds in three steps.

(a) By using (4) in connection with the inversion symmetry of the Brillouin zone, we notice that (7) solely depends on the imaginary part of the product of the three momentum matrix elements.

(b) Next, we decompose the energy denominators according to

$$\begin{aligned}D_1&=\frac{1}{E_n-E_m-i\delta}=\frac{P}{E_n-E_m}+i\pi\delta(E_n-E_m)\,,\\ D_2&=\frac{1}{E_n-E_l+\hbar\Omega-i\delta}=\frac{P}{E_n-E_l+\hbar\Omega}+i\pi\delta(E_n-E_l+\hbar\Omega)\,,\end{aligned}\tag{8}$$

where the symbol P stands for principal value in k integration. Remembering (a), we conclude that solely the imaginary part of $D_1^*D_2$ contributes to the SCPVC,

$$\mathrm{Im}(D_1^*D_2)=\pi\frac{P}{E_n-E_l+\hbar\Omega}\delta(E_n-E_m)+\pi\frac{P}{E_n-E_m}\delta(E_n-E_l+\hbar\Omega)\,. \tag{9}$$

(c) Because the first term in (9) is symmetric with respect to m,n, whereas the imaginary part of the product of the three momentum matrix elements is antisymmetric in m,n, the first term in (9) does not contribute to (7). From this property we conclude that band degeneracies, i.e., $\vec{k}$ points where $E_n(\vec{k})=E_m(\vec{k})$ (which accidentally may occur or be a consequence of crystal symmetry), do not play a special role when analyzing (7).

Executing steps (a)–(c) and performing the sum over $\Omega=\pm\omega$ we finally obtain:

$$\vec{j}=I_0\frac{|e|^3}{4\pi^2m_0^3\epsilon_0c\eta\omega^2}\sum_{l,n}\int_{\text{first BZ}}d^3k(f_n-f_l)\delta(E_n-E_l-\hbar\omega)\,\mathrm{Im}[\langle n,\vec{k}|\vec{e}\cdot\vec{p}|l,\vec{k}\rangle\langle l,\vec{k}|(\vec{e}\cdot\vec{p})S_{n,\vec{k}}\vec{p}+\vec{p}S_{l,\vec{k}}(\vec{e}\cdot\vec{p})|n,\vec{k}\rangle]\,, \tag{10}$$

where the operators $S_{\rho,\vec{k}}$, $\rho=l,n$ are defined by

$$S_{\rho,\vec{k}}=\sum_{m(\neq\rho)}\frac{|m,\vec{k}\rangle\langle m,\vec{k}|}{E_\rho-E_m}\,. \tag{11}$$

In case of band degeneracies, the $\vec{k}$ integral in (10) is defined as its principal value.

It is remarkable that in a two-band approximation, (10) may lead to a nontrivial result provided the direction of the SCPVC density is not parallel to the polarization direction of the radiation. For instance, for transitions from a completely occupied valence band, labeled by v, to an empty conduction band c, the sum over intermediate states in (11) reduces to a single term and (10) immediately leads to

$$\vec{j}\approx I_0\frac{|e|^3}{4\pi^2m_0^2\epsilon_0c\hbar^2\eta\omega^3}\int_{\text{first BZ}}d^3k\,\delta(E_c-E_v-\hbar\omega)\,\vec{e}\cdot\vec{\nabla}_{\vec{k}}[E_c(\vec{k})-E_v(\vec{k})]\,\mathrm{Im}(\langle c,\vec{k}|\vec{e}\cdot\vec{p}|v,\vec{k}\rangle\langle v,\vec{k}|\vec{p}|c,\vec{k}\rangle)\,. \tag{12}$$

Notice that the integrand of (12) is an even function of $\vec{k}$. Therefore, in general, there will be a BPVE for $\vec{j}\perp\vec{e}$, provided the respective component of the photovoltaic tensor exists by reason of crystal symmetry.

As there is no energy selection rule in (11) in connection with the participation of states $|m,\vec{k}\rangle$, a great number of virtual transitions from valence and conduction band to other bands may contribute significantly to the BPVE in a pure crystal. In particular, these virtual transitions are important for a possible explanation of an intrinsic BPVE when $\vec{j}$ and $\vec{e}$ are parallel as observed, e.g., in $BaTiO_3$.[4] Remember that a two-band approximation of (10), as given by (12), trivially would lead to $\vec{j}=0$ in this case because the imaginary part of the parentheses in (12) vanishes identically.

Fortunately, summation over bands m can be exactly performed by identification of

$$\phi^{\nu}_{\rho,k}(\vec{r}) = \sum_{m\neq\rho} \frac{\langle m,\vec{k}|\lambda p_\nu|\rho,\vec{k}\rangle}{E_\rho - E_m}\psi_{m,\vec{k}}(\vec{r}) \tag{13}$$

with the first-order pertubation correction[17] of the Bloch-wave function

$$\psi_{\rho,\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{\rho,\vec{k}}(\vec{r}) \tag{14}$$

with respect to the interaction Hamiltonian λp_ν

$$\begin{aligned}&\tilde{H} = H + \lambda p_\nu\,,\\ &\tilde{H}\tilde{\psi}_{\rho,\vec{k}}(\vec{r}) = \tilde{E}_\rho(\vec{k})\,\tilde{\psi}_{\rho,\vec{k}}(\vec{r})\,.\end{aligned} \tag{15}$$

λ is a fictitious parameter. We put $\lambda=1$ at the end of the calculation.

Trivially, the eigenstates of $\tilde{H}$ can be found by unitary transformation

$$\tilde{\psi}_{\rho,\vec{k}}(\vec{r}) = U\psi_{\rho,\vec{\kappa}}(\vec{r})\,,\quad U=\exp(-im_0\lambda x_\nu/\hbar) \tag{16}$$

with $\vec{\kappa}$ properly chosen as

$$\vec{\kappa} = \vec{k} + m_0\lambda\vec{e}_\nu/\hbar \tag{17}$$

in order to guarantee that $\tilde{\psi}_{\rho,\vec{k}}(\vec{r})$ as well as $\phi^{\nu}_{\rho,\vec{k}}(\vec{r})$ are Bloch functions belonging to wave vector $\vec{k}$.

Expanding $\tilde{\psi}_{\rho,\vec{k}}(\vec{r})$ in powers of λ and keeping in mind that $\phi^{\nu}_{\rho,\vec{k}}(\vec{r})$ is orthogonal to $\psi_{\rho,\vec{k}}(\vec{r})$, we obtain

$$\phi^{\nu}_{\rho,\vec{k}}(\vec{r}) = \lambda(m_0/\hbar)e^{i\vec{k}\cdot\vec{r}}\left(\frac{\partial}{\partial k_\nu}u_{\rho,\vec{k}}(\vec{r}) - u_{\rho,\vec{k}}(\vec{r}) \times \int_{\text{unit cell}} u^{*}_{\rho,\vec{k}}(\vec{r}\,')\frac{\partial}{\partial k_\nu}u_{\rho,\vec{k}}(\vec{r}\,')d^3r'\right). \tag{18}$$

Inserting (11) in (10) and using (13) and (18) we obtain our main result for the representation of the SCPVC density

$$\vec{j} = I_0\frac{|e|^3}{4\pi^2 m_0^2\epsilon_0 c\hbar\eta\omega^2}\sum_{l,n}\int_{\text{first BZ}} d^3k(f_n - f_l)\delta(E_n - E_l - \hbar\omega)\,\mathrm{Im}[\langle n,\vec{k}|\vec{e}\cdot\vec{p}|l,\vec{k}\rangle\langle l,\vec{k}|(\vec{e}\cdot\vec{p})\vec{R}_{n,\vec{k}} + \vec{R}^{*}_{l,\vec{k}}(\vec{e}\cdot\vec{p})|n,\vec{k}\rangle]\,. \tag{19}$$

The objects

$$\vec{R}_{\rho,\vec{k}}(\vec{r}) = \frac{\nabla_{\vec{k}}u_{\rho,\vec{k}}(\vec{r})}{u_{\rho,\vec{k}}(\vec{r})} - \int_{\text{unit cell}} u^{*}_{\rho,\vec{k}}(\vec{r}\,')\nabla_{\vec{k}}u_{\rho,\vec{k}}(\vec{r}\,')d^3r' \tag{20}$$

are closely related to the crystal momentum representation of the position operator which has been studied in detail by Adams[18] and Blount.[19] In deriving (18)–(20), we implicitly assumed differentiability of $\psi_{n,\vec{k}}(\vec{r})$ with respect to $\vec{k}$. Then (19) is independent of the choice of phases of the Bloch functions. We also note that the integral in (20) is purely imaginary[18]; thus, it contributes to (19).

As far as we can see, general symmetry properties of Bloch states do not force (19) to vanish identically. In particular, from time-reversal symmetry, we can only conclude that the following symmetry relation of matrix elements, analogous to (4), holds:

$$\vec{M}_{l,n}(\vec{k}) = \langle l,k|(\vec{e}\cdot\vec{p})\vec{R}_{n,\vec{k}}|n,\vec{k}\rangle = \vec{M}^{*}_{l,n}(-\vec{k})\,, \tag{21}$$

which has been already used in deriving (19). The reason why the reversibility of the basic microscopic equations is not maintained in the calculation of a macroscopic quantity, e.g., the SCPVC density, is known to be a consequence of the sequence in which the limits in (7) have to be performed: Firstly, we have to take the thermodynamic limit $V\rightarrow\infty$ and then let $\delta\rightarrow 0$.

If the symmetry group of the crystal contains the inversion I, we can conclude from[16]

$$I\psi_{n,\vec{k}}(\vec{r}) = \psi_{n,\vec{k}}(-\vec{r}) = \psi_{n,-\vec{k}}(\vec{r}) \tag{22}$$

that the momentum matrix elements (4) as well as (21) are real. Hence, trivially, there is no BPVE in centrosymmetric crystals. However, in noncentrosymmetric crystals and for photonenergies larger than the band gap, (19) is expected to be nonzero. In this respect, the BPVE is different from optical rectification,[21] which causes a change of the polarization only, and therefore, will not give rise to a steady-state emf or a SCPVC. In addition, optical rectification can occur even if the photon energy is smaller than the band gap.

Even though (19) gives a representation of the BPVE in terms of transitions between pairs of bands l,n, the SCPVC is exclusively determined by nondiagonal matrix elements of the current operator in the Bloch basis. Inspection of (11) leads to the conclusion that the BPVE in pure crystals is intimately related to the participation of virtual transitions from bands l and n to all bands m, upon photoexcitation of an electron from band l to n, or vice versa. Neglecting these virtual transitions will lead to the incorrect conclusion that there will be no BPVE in a pure crystal.[6-9,12,14] Unlike a conventional field or diffusion current, which is determined by the density of charge carriers and their velocity, the SCPVC in a pure crystal is related to the derivative of wave functions with respect to wave number. To our knowledge, no representation of a normal steady-state current of that type has been reported before.

Comparison of (19) with the absorption coefficient[16]

$$\alpha(\omega)=\frac{\omega}{c\eta}\,\frac{e^2}{2\pi^2\epsilon_0 m_0^2\omega^2}\sum_{n,l}\int_{\text{first BZ}} d^3k(f_n-f_l)\left|\langle\vec{k},l|\vec{p}\cdot\vec{e}|\vec{k},n\rangle\right|^2\,\delta(E_l-E_n-\hbar\omega) \tag{23}$$

reveals that the intrinsic value of the anisotropy distance $\vec{s}$ is related to an average value of the $\vec{R}$ operators

$$\vec{s}=\mathrm{Im}\langle\tfrac{1}{2}(\vec{R}_{v,\vec{k}}+\vec{R}_{c,\vec{k}})\rangle_{\mathrm{av}}\,, \tag{24}$$

where c,v label conduction and valence bands, respectively. Therefore, for transitions between bands of the same symmetry, $\vec{s}$ is expected to be rather small near the absorption edge.

III. EXPERIMENTAL SITUATION AND ESTIMATE OF THE BPVE

A. Pyroelectrics

The experimental situation concerning the existence of an intrinsic BPVE in pyroelectrics or ferroelectrics has not been completely clarified. Nevertheless, it is believed that in nominally pure $BaTiO_3$, the observed BPVE is related to interband transitions. Remarkably, there is only one investigation by Koch *et al.*,[4] who found $s \approx 2$ Å at $\hbar\omega\approx 3.4$ eV ($\lambda=370$ nm) for $\vec{j}\perp\vec{e}$ at room temperature. From several measurements reported by Krätzig and Kurz,[3,22] we likewise conclude that an intrinsic BPVE may possibly occur in $LiNbO_3$. Provided this conclusion is correct, we can estimate the intrinsic value of the anisotropy distance for $LiNbO_3$ in the vicinity of the absorption edge as $s\approx 0.2$ Å at $\hbar\omega=4$ eV, whereas $s\approx 1.5$ Å at $\hbar\omega=3.2$ eV for transitions from the ground state of Fe^{2+} dopants into the conduction-band states of $LiNbO_3$. Furthermore, we would like to draw attention to CdS, which is pyroelectric, in which an intrisic BPVE most likely has been observed by Glass.[1]

Because of the interference nature of the intrinsic BPVE, a correct estimate of the SCPVC is a delicate task. A crude estimate, however, may be obtained for a ferroelectric or pyroelectric insulator at $T=0$ provided selection rules for the transition matrix elements are not important.

(a) First, we consider the case $\vec{e}\perp\vec{j}$, where $\vec{j}$ is assumed to be parallel to the direction of the spontaneous polarization of the pyroelectric. Our estimate of the SCPVC is based on the two-band approximation (12) and, for simplicity, we will assume isotropic and parabolic conduction and valence bands centered at Γ. Furthermore, a plausible approximation of the imaginary part of the momentum matrix elements is given by

$$\mathrm{Im}\langle c,\vec{k}|p_\mu|v,\vec{k}\rangle\approx\left(\frac{\delta}{a}\right)\left|\langle c,\vec{k}|p_\mu|v,\vec{k}\rangle\right| \tag{25}$$

which may be checked, e.g., in tight binding approximation. a denotes the lattice constant and the length δ characterizes the deviation of the noncentrosymmetric crystal unit cell from its centrosymmetric configuration in the paraelectric phase. Provided (25) does not sensitively depend on μ and $\vec{k}$ near the band edge, our estimate of the anisotropy distance near the gap energy is given by

$$s_\perp\approx\frac{\hbar}{E_g}\left(\frac{\delta}{a}\right)[2(\hbar\omega-E_g)(1/m_v^*+1/m_c^*)]^{1/2}\,. \tag{26}$$

E_g denotes the gap energy and m_v^*, m_c^* are the effective valence and conduction-band masses, respectively. For photon energies not in the vicinity of the band gap, the $\vec{k}$ dependence of (25) is relevant and $s_\perp$ is expected to decrease with increasing $\hbar\omega$.

It should be noted, however, that (26) is not applicable to $BaTiO_3$ in the tetragonal phase. Because of the symmetry of the valence and conduction bands,[20] one of the two matrix elements in (12) is always zero and, hence, at least three bands are needed to get a nontrivial result for $s_\perp$.

(b) Second, for $\vec{e}\,\|\,\vec{j}$ the BPVE is exclusively determined by virtual transitions between conduction or valence band and other bands. In this case, we start from (10) and approximate the operator $S_{v,\vec{k}}$ by

$$\begin{aligned}S_{v,\vec{k}}&\approx-\frac{1}{E_g}|c,\vec{k}\rangle\langle c,\vec{k}|-\frac{1}{E_{gv}}\sum_{m\neq v,c}|m,\vec{k}\rangle\langle m,\vec{k}|\\&\approx-\frac{1}{E_{gv}}\underline{1}_{\vec{k}}+\frac{1}{E_{gv}}|v,\vec{k}\rangle\langle v,\vec{k}|+\left(\frac{1}{E_{gv}}-\frac{1}{E_g}\right)|c,\vec{k}\rangle\langle c,\vec{k}|\end{aligned} \tag{27}$$

E_{gv} denotes an average gap between the valence band and bands above the conduction band, and

$$\underline{1}_{\vec{k}}=\sum_m|m,\vec{k}\rangle\langle m,\vec{k}| \tag{28}$$

denotes the identity operator in the subspace of Bloch states belonging to the same wave vector. When $S_{c\vec{k}}$ is approximated in the same manner, we arrive at

$$\vec{j}_{\parallel} \approx I_0 \frac{|e|^3}{4\pi^2 m_0^3 \epsilon_0 c \eta \omega^2} \int_{\text{first BZ}} d^3k\, \delta(E_c - E_v - \hbar\omega)(-1/E_{gv} - 1/E_{gc})\, \mathrm{Im}(\langle v,\vec{k}|p_{\parallel}|c,\vec{k}\rangle\langle c,\vec{k}|p_{\parallel}^2|v,\vec{k}\rangle)\,. \tag{29}$$

Notice that projection operators $|v,\vec{k}\rangle\langle v,\vec{k}|$ and $|c,\vec{k}\rangle\langle c,\vec{k}\rangle$ in (27) do not contribute to $\vec{j}_{\parallel}$.

By using the same approximations as stated in (a), we obtain

$$s_{\parallel} \approx \frac{\delta}{a}\left(\frac{1}{E_{gv}} + \frac{1}{E_{gc}}\right) E_g \frac{a}{\pi} M(\omega)\,, \tag{30}$$

where the function $M(\omega)$, defined by

$$M(\omega) = \frac{\pi\hbar}{a m_0 E_g} \frac{|\langle c,\vec{k}|p_{\parallel}^2|v,\vec{k}\rangle|}{|\langle c,\vec{k}|p_{\parallel}|v,\vec{k}\rangle|} \tag{31}$$

is of order unity for $\hbar\omega > E_g$. This can be checked, e.g., in tight-binding approximation or for the Kronig-Penney model.

For a ferroelectric or pyroelectric insulator, plausible values for the parameters needed to evaluate (26) and (30) are $a \approx 3$ Å, $E_g \approx 3$ eV, $E_{gv} > E_{gc} \approx 1$ eV, $m_v \approx m_c \approx m_0$, and $\delta/a \approx 0.05$. These lead to $s_{\perp} \approx 0.1$ Å (at $\hbar\omega - E_g \approx 0.5$ eV) and $s_{\parallel} \approx 0.2$ Å. Symbols $\parallel$ and $\perp$ refer to the polarization direction of the radiation with respect to the spontaneous polarization. As $s_{\parallel} > s_{\perp}$, whereas $s_{\parallel} = 0$ according to (12) in a two-band approximation, virtual transitions to upper conduction bands are expected to be likewise important for $\vec{e} \perp \vec{j}$ and $\vec{e} \parallel \vec{j}$. In conclusion, our estimated value of the anisotropy distance seems to be of the correct order of magnitude when compared with the data for $LiNbO_3$ but, surprisingly, our estimate is smaller by one order of magnitude for $BaTiO_3$, where $s_{\perp} \approx 2$ Å is the experimental result. Because of the crude approximations used in deriving (26) and (30), this discrepancy should not be taken too seriously.

B. Piezoelectrics

In contrast to a ferroelectric or pyroelectric crystal, a nonpyroelectric piezoelectric crystal has no *a priori* direction for the SCPVC. Nevertheless, symmetry considerations do not rule out the possibility of the BPVE in these materials, provided the polarization direction of the radiation is not parallel to one of the crystal axes. This property has also been noted by Baskin *et al.*,[9] who studied the case of asymmetric photoexcitation and capture from and to impurities in a piezoelectric crystal.

In order to demonstrate that there may be a nonzero SCPVC in nonpyroelectric piezoelectrics, we consider GaAs or GaP, which are noncentrosymmetric cubic crystals with point group $43m$ (Ref. 23) for which the only nonvanishing components of the photovoltaic tensor are

$$P_{xyz} = P_{xzy} = \gamma(\omega) \tag{32}$$

and all cyclic permutations of indices.[24] We assume that the radiation is polarized perpendicular to the x axis under an angle φ to the z axis. Using (2) and (32), the components of the SCPVC are given by

$$j_x = I_0 \gamma(\omega) \sin(2\varphi)\,, \quad j_y = j_z = 0\,. \tag{33}$$

In this example, the direction of the SCPVC is parallel or antiparallel to the crystal x axis and, remarkably, the SCPVC will change its sign if the polarization direction of the radiation will be turned by 90 degrees.

It should be stressed that the SCPVC solely depends on the polarization direction of the radiation, but it does not depend on the propagation direction of the radiation. Therefore, it is not necessary that the propagation direction of the radiation is parallel to the crystal x axis but it may have any direction perpendicular to the $\vec{e}$ direction. In this respect, the BPVE is essentially different from the photon drag effect,[10,11] cf. (2), or the Dember effect in the interpretation of Landau.[25]

There are several experimental investigations on radiation-induced emf's in nonpyroelectrics piezoelectrics, e.g., on Te,[10,26] GaP,[11] and GaAs.[27] Unfortunately, their connection with the BPVE in pyroelectrics has not been recognized; only Ivchenko and Pikus[8] refer to these papers. The reason may be that the corresponding authors use the terminology "optical rectification." Nevertheless, Ribakovs and Gundjian[10] and Gibson *et al.*,[11,28] definitely know that the reported phenomenon could not originate from a change in polarization, but stems from a nonlinear conductive behavior of their crystals. For instance, in n-doped GaP with $n = 2.4 \times 10^{16}$ cm^{-3}, the BPVE is largest at $\lambda \simeq 3$ μm, leading to a SCPVC of about $j_{sc} \approx 0.7 \times 10^{-6}$ A cm^{-2} for $I_0 = 1$ watt cm^{-2}, i.e., $\gamma \approx 10^{-6}$ V^{-1}. In this case, the anisotropy distance, $s \approx 7.5$ Å, is even larger than $a = 5.45$ Å, the lattice constant of GaP. We have not yet succeeded, however, to work out an estimate for the BPVE in piezoelectrics.

IV. DISCUSSION AND CONCLUSIONS

As the BPVE in a pure crystal is determined by virtual transitions, i.e., nondiagonal matrix elements of the current operator, the SCPVC cannot be represented in the form

$$\vec{j} = -|e| \sum_{\vec{k},n} f_n(\vec{k})\vec{v}_n(\vec{k}) ,$$
$$\vec{v}_n(\vec{k}) = \frac{1}{\hbar}\nabla_{\vec{k}} E_n(\vec{k}) , \tag{34}$$

which is generally assumed to hold for a normal metal or a semiconductor, $\vec{v}_n(\vec{k})$ denoting the velocity and $f_n(\vec{k})$ the density of electrons in band n and with wave vector $\vec{k}$. Instead of (34) one ought to use the exact relation

$$\vec{j} = \mathrm{Tr}(\rho j_{op}) \equiv \sum_{\alpha} \langle \alpha | \rho \vec{j}_{op} | \alpha \rangle = \sum_{\alpha\alpha'} \langle \alpha | \rho | \alpha' \rangle \langle \alpha' | \vec{j}_{op} | \alpha \rangle , \tag{35}$$

where ρ denotes the statistical operator, $\vec{j}_{op}$ denotes the current operator, and $|\alpha\rangle$ denotes an arbitrary complete set of (N electron) states.

In order to demonstrate that contributions from nondiagonal matrix elements of $\vec{j}_{op}$ are by no means peculiar or even metaphoric, we shall consider a single electron in a crystal and specify states $|\alpha\rangle$ to momentum eigenstates $|\vec{p}\rangle$ and Bloch states $|\vec{k},n\rangle$, respectively. Taking into account that $\vec{j}_{op} \sim \vec{p}$, where the term containing the vector potential can be neglected in the dipole approximation, we obtain in the momentum basis

$$\vec{j} = -|e| \sum_{p} \frac{\vec{p}}{m_0} \frac{1}{V} \langle \vec{p} | \rho | \vec{p} \rangle , \tag{36}$$

which is exactly of the form (34). In Bloch representation, however, one necessarily gets terms which are nondiagonal with respect to the band index.

$$\vec{j} = -|e| \sum_{k,n} \frac{1}{V} \langle \vec{k},n | \rho | \vec{k},n \rangle \vec{v}_{\vec{k},n} - \frac{|e|}{m_0 V} \times \sum_{\vec{k}} \sum_{n \neq n} \langle \vec{k}n | \rho | \vec{k}n' \rangle \langle \vec{k}n' | \vec{j}_{op} | \vec{k}n \rangle . \tag{37}$$

Very often the diagonal terms in (37) give the dominant contribution to the current and the nondiagonal matrix elements merely lead to "local field corrections." For instance, this approximation is well justified if the SCPVC is due to an asymmetry in the photo cross section for electron emission from a bound state of an impurity atom into the conduction-band states of the crystal. Denoting by $|\psi(t)\rangle$ the exact state of the electron in the crystal under the influence of the radiation field, we can calculate the diagonal elements of ρ, $f_n(\vec{k}) \sim |\langle \psi(t) | \vec{k},n \rangle|^2$ by means of transition probabilities which trivially would explain that $j_{s\tilde{c}} \sim I_0\tau$, where τ is the momentum relaxation time of photoelectrons.[6-9,12,29] However, even in the impurity case, the interference terms in (37) are important near the absorption edge.[5] (It has been stressed by Belinicher *et al.*,[6,7,13] that interference terms may also be responsible for asymmetric scattering of electrons by impurities and phonons.)

During completion of our work two papers by Kristoffel and Gulbis[30,31] appeared which presented an analytic calculation of the SCPVC in tetragonal $BaTiO_3$ by using a three-band approximation of (7). These authors found that magnitude as well as spectral dependence of their calculated $\kappa_\perp(\omega)$ agrees fairly well with experimental results reported by Koch *et al.*[4] This gives further support to the existence of an intrinsic BPVE in $BaTiO_3$.[32] Surprisingly, $\kappa_\parallel(\omega) \equiv 0$ in this three-band approximation. Nevertheless, we believe that an evaluation of the exact formulas for the SCPVC given by (10) and (19) would lead to a nonzero $\kappa_\parallel(\omega)$, which, however, may be much smaller than $\kappa_\perp(\omega)$. Therefore, the observed $\kappa_\parallel(\omega)$ may be dominated by impurity transitions, since the impurity model which we proposed earlier[5] reproduces the complicated spectral dependence of the observed $\kappa_\parallel(\omega)$ quantitatively.

Besides $\kappa_\parallel$ and $\kappa_\perp$, there is a third independent component of the photovoltaic tensor of $BaTiO_3$ which has been overlooked up to now. The symmetry of the ferroelectric phase of $BaTiO_3$ in the temperature range 5°–120 ℃ is tetragonal with the point group $4mm$ (Ref. 33) and, thus, the photovoltaic tensor has the following independent nonvanishing components[24]

$$P_{xxz} = P_{xzx} = P_{yyz} = P_{yzy} \, ; \; P_{zxx} = P_{zyy} \, ; \; P_{zzz} \, , \tag{38}$$

where the polar axis is assumed to be parallel to the z axis. $\kappa_\parallel$ and $\kappa_\perp$ are related to P_{zzz} and P_{zxx}, respectively. The third independent component of P, P_{xxz} say, is related to components of the SCPVC perpendicular to the spontaneous polarization. This current component will be induced by radiation whose polarization vector lies in the x-z or y-z plane, respectively. A sinusoidal variation of the respective x or y components of the SCPVC density with polarization angle, analogous to (33) is predicted. However, only a detailed numerical analysis of (19) by using the correct band structure and Bloch functions of $BaTiO_3$ and other ferroelectric or piezoelectric materials can answer the question about the magnitude and spectral dependence of the intrinsic BPVE. Such a program will be of great importance for a deeper understanding of the BPVE in pure crystals.

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