Anomalous bulk photovoltaic effect in ferroelectrics:
A quadratic response theory

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We present a phenomenological description and a quantum-mechanical theory of electron transport in the anomalous bulk photovoltaic effect (ABPVE) in ferroelectrics. Our theory is based on a quadratic response formalism which leads to an exact expression for the short-circuit photovoltaic current (SCPVC). This theory indicates the existence of an ABPVE even in a system of pure Bloch states. We demonstrate the capability of our theory by performing an explicit calculation of the SCPVC for a one-dimensional model of independent impurities. From these results we conclude that sign changes of the SCPVC, as observed in $BaTiO_3$, are either due to impurities which have a bound excited state, or to Bloch states with two or more overlapping valence or conduction bands. There is evidence for both mechanisms.

I. INTRODUCTION

Homogeneous illumination of ferroelectric single crystals leads to a stationary short-circuit photovoltaic current (SCPVC) parallel to the direction of the polar crystal axis.[1-4] In contrast to the photovoltaic effect occurring in p-n junctions, or metal-semiconductor boundaries,[5] this phenomenon is a bulk property of the ferroelectric, in which charge carriers are transported without the existence of a gradient in the electrochemical potential.[2-4]

Experimental results for the SCPVC are usually presented in the following form[1,3,4]:

$$j_{sc}(\omega) = \kappa(\omega)\alpha(\omega)I_0 \equiv e\alpha(\omega)(I_0/\hbar\omega)s(\omega) , \quad (1)$$

where ω denotes the frequency, I_0 denotes the intensity of the radiation, $\alpha(\omega)$ is the absorption constant of the crystal, $\kappa(\omega)$ denotes Glass's anisotropy function, and $s(\omega)$ denotes the anisotropy distance. $j_{sc}(\omega)$, $\kappa(\omega)$, and $s(\omega)$ depend on ω, as well as on the polarization direction of the light which indicates that the SCPVC is directly related to the optical-excitation process.[2-4] Under open-circuit conditions, anomalous large photovoltages of more than 1 kV have been reported.[6,7] A more detailed collection of the properties of this anomalous bulk photovoltaic effect (ABPVE) may be found, e.g., in Ref. 8.

At present, there are several different models for the ABPVE. The most convincing one is due to Glass et al.[1] who divided the electronic processes into two steps: ionization of charge carriers from a bound state into delocalized states in connection with an asymmetry in the photo cross section and a subsequent diffusion of the carriers through the crystal. Theoretical investigations based on this model have

been published by Belinicher et al.,[9] Baskin et al.,[10] Heyszenau,[11] and by the present authors.[8,12] In particular, Heyszenau[11] carefully analyzed this model and investigated the SCPVC and the photo emf. But in contrast to Ref. 11, we believe that violation of time-reversal symmetry, which is present in every irreversible phenomenon, is merely one of many other necessary conditions for the ABPVE. We believe that the existence of a radiation-induced direct current is essentially due to violation of spatial inversion symmetry. For instance, in the normal photoeffect, the current is directly connected with the existence of a free crystal surface which breaks spatial inversion symmetry. In the ABPVE, the momentum imbalance of the photoemitted electron is due to a quantum-mechanical interference effect[8] which is triggered by the short-range electric-field components in a spatially nonsymmetric crystal. This effect is closely related to the electrical Bohm-Aharanov effect.[13]

Glass and Chanussot[14] have shown theoretically that there is an asymmetry in the transition probability even for interband optical transitions in pure crystals, when taking into account a Frank-Condon relaxation of the excited state following excitation.

An alternative model has been proposed by Koch et al.,[2] explaining the ABPVE by coupling electrons to photoinduced polarization fluctuations. Another different mechanism for the ABPVE which is based on rather special electron-phonon effects has been proposed recently by Chanussot.[15] But up to now, it is an open question whether or not these mechanisms would lead to a stationary photocurrent.

It is the purpose of this paper to present an exact microscopic theory of the ABPVC which is based on

the quantum states of the system. This theory does not *a priori* contain a separation of electronic processes in two distinct steps as the Glass model does. In contrast to previous theories,[9,11] our theory indicates the existence of the ABPVE even in a system of pure Bloch states with assistance of a damping mechanism. To demonstrate the capability of our theory, we shall perform an explicit calculation of the SCPVC for a one-dimensional system of acentric impurities which has been already used in Ref. 12. Preliminary results have been reported in Ref. 16.

II. PHENOMENOLOGICAL THEORY OF THE ABPVE

Within a phenomenological theory, the ABPVE is directly related to a quadratic term in the functional relation between the current density $\vec{j}(\vec{r},t)$ and the electric field $\vec{E}(\vec{r},t)$ of the radiation. In addition, we shall postulate this relation to be local and causal, and we shall neglect the influence of the magnetic field of the radiation. Provided there is no gradient in the electrochemical potential η, this relation reads

$$j_\nu(\vec{r},t) = \sum_\mu \int_{-\infty}^t dt' \, \sigma_{\mu\nu}^{(1)}(t-t') E_\mu(\vec{r},t')$$
$$+ \sum_{\lambda,\mu} \int_{-\infty}^t dt' \int_{-\infty}^{t'} dt'' \, \sigma_{\lambda\mu\nu}^{(2)}(t-t';t'-t'')$$
$$\times E_\lambda(\vec{r},t') E_\mu(\vec{r},t'') \quad . \quad (2)$$

λ, μ, ν refer to cartesian components, and $\sigma^{(1)}$, $\sigma^{(2)}$ denote the linear and quadratic conductivity tensors in the time domain. The SCPVC is given by the dc component of Eq. (2). For a monochromatic plane wave with frequency ω, which is linearly polarized parallel to one of the coordinate axis, we obtain

$$j_{sc,\nu}(\omega) = \frac{1}{2} E_{0,\mu}^2 \int_0^\infty ds \int_0^\infty ds' \, \sigma_{\mu\mu\nu}^{(2)}(s,s') \cos(\omega s') \quad ,$$
$$(3)$$

$$I_0 = \frac{1}{2} \epsilon^{1/2} \epsilon_0 c E_{0,\mu}^2 \quad . \quad (4)$$

c denotes the speed of light, ϵ denotes the dielectric constant of the crystal, and $\vec{E}_0$ is the amplitude of the electric field of the radiation.

It is remarkable that $\vec{j}_{sc}$ is not directly related to the absorbed energy which is soley determined by $\sigma^{(1)}$, i.e.,

$$\dot{w} \equiv \langle \vec{j} \cdot \vec{E} \rangle_{av} = \frac{1}{2} E_{0,\mu}^2 \int_0^\infty \sigma_{\mu\mu}^{(1)}(s) \cos(\omega s) \, ds \quad , \quad (5)$$

where $\langle .... \rangle_{av}$ means "time average". Nevertheless absorbed energy may not be identical with dissipated energy which can also be associated with $\sigma^{(2)}$. Therefore, the SCPVC may very well be accompanied by entropy production although the standard relation[17]

$$\dot{S} = \vec{j}_{sc} \cdot \vec{X}, \quad \vec{X} \sim \nabla \eta \quad (6)$$

leads to $\dot{S} = 0$ if we have $\vec{X} = 0$. Because there is no simple relationship between $\sigma^{(1)}$ and $\sigma^{(2)}$, a factorization of $j_{sc}(\omega)$ in terms of $\alpha(\omega)$ and $\kappa(\omega)$ [as it is used in Eq. (1)] does not lead to a deeper insight into the mechanisms of the ABPVE, than does the quantity $j_{sc}(\omega)$ itself. Moreover the electromagnetic energy density which is absorbed by the crystal per unit time is not strictly determined by $\alpha(\omega)$ but by the real part of the conductivity, i.e., Eq. (5).

For inhomogeneous situations, we include in $\vec{E}(\vec{r},t)$ a static electric field $\vec{E}_{st} = -\nabla\phi_{st}$ and add a diffusion term (grad ζ) on the right-hand side of Eq. (2). In this case, the photocurrent is given by

$$\vec{j}_{ph} = (1/e) \, \sigma_{ph}(I_0) \nabla\eta + \vec{j}_{sc} \quad , \quad (7)$$

$$\eta = -e\phi_{st} + \zeta \quad , \quad (8)$$

where σ_{ph} denotes the photoconductivity, ϕ_{st} denotes the electrical potential, ζ denotes the chemical potential of the charge carriers, and j_{sc} is short for the right-hand side of Eq. (3). Because E_{st} can come close or even reaches the field strength of dielectric breakthrough, nonlinear terms in the photoconductivity should be included too.

Under open-circuit conditions a photovoltage U_{ph} (photo emf) appears, which is given by the difference in η at both contacts, at $z = 0$ and $z = L$. L denotes the length of the illuminated part of the crystal. Putting $j_{ph} = 0$ in Eq. (7) and integrating, we obtain

$$U_{ph} \equiv -\frac{1}{e}[\eta(0) - \eta(L)] = j_{sc}L/\sigma_{ph}(I_0) \quad . \quad (9)$$

Relation (9) is already known and has been confirmed in several experiments, e.g., Refs. 3 and 4. Because the photovoltaic current is imposed on the crystal, U_{ph} may become very large in materials with low photoconductivity. An extraordinary example is ferroelectric potassium dihydrogen phosphate (KDP) where Fridkin[7] measured photovoltages larger than 10^5 volts!

The quadratic term in Eq. (2) is analogous to the quadratic relationship between the induced polarization $\vec{P}(\vec{r},t)$, and $\vec{E}(\vec{r},t)$ which is commonly used in the theory of nonlinear optics, e.g., Ref. 18. However, there is an essential difference. The stationary polarization response which is known as "optical rectification"[18,19] leads neither to a steady-state open-circuit voltage, nor a short-circuit current. Because of $\vec{j}_{sc} \sim \dot{\vec{P}}$ the latter requires a component in $\vec{P}$ which linearly increases with time.

In a crystal whose symmetry group contains the inversion, all components of $\sigma^{(2)}$ are zero[20]; hence we have $\vec{j}_{sc} = 0$. But until now it is an open question if absence of inversion symmetry will be a sufficient condition for the ABPVE. In experiments, the situation is even more complicated because there may be

a surface photovoltaic effect even though the crystal has inversion symmetry. Such an effect has been discovered by Ruppel and Grant[21] in single crystals of orthorhombic sulphur.

III. QUANTUM-MECHANICAL REPRESENTATION OF THE SCPVC

In this section we shall present a microscopic theory for the SCPVC by applying standard methods to calculate nonlinear susceptibilities, e.g., Ref. 18.

In thermal equilibrium, the density operator $\rho(t)$ of the system with Hamiltonian H_0 and electron number N is given by

$$\rho_0 = Z^{-1} \exp[-\beta(H_0 - \zeta N)] \quad , \tag{10}$$

where we have $\beta = 1/k_B T$, and Z denotes the grand-canonical partition function. There is no current associated with Eq. (10).

By switching on the illumination at $t = 0$, $\rho(t)$ evolves in time according to

$$i \hbar \dot{\rho}(t) = [H, \rho] - i \hbar (\rho - \rho_0)/\tau \quad , \tag{11}$$

$$H = H_0 + V(t) \quad , \tag{12}$$

where $V(t)$ describes the interaction between the electrons and the electromagnetic field. We rely on the electric dipole approximation for electronic transitions, and we shall therefore neglect spatial variations of the vector potential $\vec{A}(\vec{r}, t)$ of the radiation. By choice of gauge, the scalar potential is zero, i.e.,

$$\vec{A}(t) = (\vec{E}_0/\omega)\cos\omega t \quad , \tag{13}$$

$$V(t) = \vec{J} \cdot \vec{A} + e^2/(2m_0 V)\vec{A}^2 \quad , \tag{14}$$

$$\vec{J} = -(e/Vm_0) \sum_{i=1}^{N} \vec{p}_i \quad . \tag{15}$$

V denotes the volume of the crystal. Because I_0 is rather large in experiments, we shall treat $\vec{A}(t)$ as a classical field. m_0 denotes the mass and $\vec{p}$ the momentum of an electron. The second term on the right-hand side of Eq. (11) describes a constant relaxation rate in time τ of the system towards thermal equilibrium. If H_0 includes inelastic electron-phonon processes, one will be allowed to let $\tau \to \infty$ at the end of the calculation. Otherwise a finite τ approximately describes the energy transfer from the combined system "electrons plus radiation" to the heat bath.

To calculate the current density which is induced by the incident radiation

$$j(t) = \text{Tr}[\rho(t)\vec{J}_A] \tag{16}$$

$$\vec{J}_A = \vec{J} - (e/m_0)\vec{A} \tag{17}$$

we transform Eq. (11) into an integral equation and solve it by iteration

$$\rho(t) = \rho_0 + \rho_1(t) + \rho_2(t) + \dots \quad , \tag{18}$$

$$\rho_{n+1}(t) = -\frac{i}{\hbar} \int_0^t ds \exp\left[\frac{-s}{\tau}\right] U(s)$$

$$\times [\rho_n(t), V(t-s)] U^\dagger(s) \quad . \tag{19}$$

$U(s)$ denotes the time-evolution operator of the system without illumination

$$U(s) = \exp(-itH_0/\hbar) \quad . \tag{20}$$

The part of Eq. (16) which is linear in I_0, solely depends on $\rho_2(t)$. The second terms on the right-hand side of Eqs. (14) and (17) do not contribute to $\vec{j}_{sc}$. By letting $t \gg \tau$ in Eq. (16) we obtain the dc component in terms of $\sigma^{(2)}$.

$$\sigma^{(2)}_{\mu\mu\nu} = -(V/\hbar\omega)^2 \exp[-(s+s')/\tau]$$

$$\times \text{Tr}(\rho_0 \{J_\mu(0), [J_\mu(s), J_\nu(s+s')]\}) \quad . \tag{21}$$

$\vec{J}(s)$ denotes the current operator in the Heisenberg picture at time s, i.e.,

$$\vec{J}(s) = U(s)\vec{J}U^\dagger(s) \tag{22}$$

Relation (21) together with Eq. (3) ought to be the basis of theoretical investigations of the ABPVE. However, the evaluation of the three-current correlation function ("three-photon vertex") will be even more laborious than the evaluation of the linear conductivity when starting from the Kubo formula.

If a one-particle approximation with states $|n\rangle$ and energies E_n is applicable, Eq. (21) can be simplified considerably by

$$H_0 = \sum_n E_n C_n^\dagger C_n \quad , \tag{23}$$

$$\vec{J} = -\left(\frac{e}{m_0 V}\right) \sum_{n,n'} \langle n'|\vec{p}|n\rangle C_{n'}^\dagger C_n \quad , \tag{24}$$

where $C_n^\dagger, C_n$ denote creation and annihilation operators for fermions. Inserting Eqs. (10), (23), and (24) into Eq. (21) and using Eq. (3) we obtain by standard operator techniques

$$j_{sc,\nu}(\omega) = -\frac{I_0(e/m_0)^3}{2V\epsilon^{1/2}\epsilon_0 c\,\omega^2}\sum_{l,m,n}\sum_{\Omega=\pm\omega}(f_n-f_l)\frac{\langle n|p_\mu|l\rangle}{E_n-E_l+\hbar\Omega-i\hbar/\tau}\left[\frac{\langle l|p_\mu|m\rangle\langle m|p_\nu|n\rangle}{E_n-E_m-i\hbar/\tau}-\frac{\langle l|p_\nu|m\rangle\langle m|p_\mu|n\rangle}{E_m-E_l-i\hbar/\tau}\right].$$

$$(25)$$

f_n is the Fermi distribution function

$$f_n = \{1+\exp[\beta(E_n-\zeta)]\}^{-1} \; . \qquad (26)$$

Figure 1 sketches the mathematical structures of Eq. (25).

Equations (21) and (25) are formally identical with the representation of the current in the theory of the external photoeffect, e.g., Refs. 22 and 23. But in contrast to the ABPVE, the external photoeffect is intimately connected with the existence of a free crystal surface.

IV. SOME PROPERTIES OF $j_{sc}(\omega)$

From Eqs. (21) and (25) we can find criteria for the existence of the ABPVE and some spectral properties of the SCPVC. For instance,

(i) In systems with spatial inversion symmetry, we necessarily have $\bar{j}_{sc}=0$. This property is already known from Sec. II and can be rediscovered from Eq. (21) by performing the following operations: (I denotes the inversion operator with $[H_0,I]=0$.)

We insert the identity II^{-1} between every two operators in the argument of the trace,commute I and ρ_0, and use the cyclic property of the trace. Because $\vec{J}$ changes sign under I, we immediately arrive at $\sigma^{(2)}=-\sigma^{(2)}$. This implies we have $\sigma^{(2)}=0$ and $j_{sc}=0$.

(ii) A two-band approximation of the complete set of Bloch states in a pure crystal likewise leads to $j_{sc}=0$, even when the symmetry group of the crystal does not contain the inversion. This result has been first published by Belinicher et al.[9] by using the Glass model.
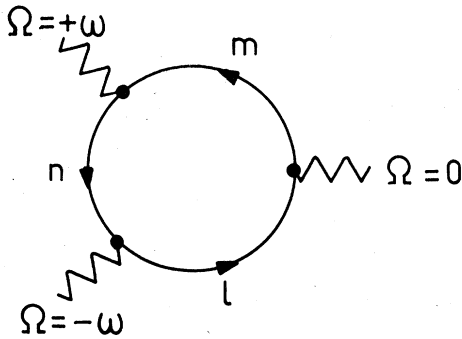

FIG. 1. Graphical illustration of transitions which contribute to the ABPVE by using a one-particle approximation.

In our theory, this result follows directly from Eq. (25) by using the following relations for Bloch states which hold irrespective of crystal symmetry[24]:

$$\langle \vec{k}', \alpha'|\vec{p}|\vec{k}, \alpha\rangle = \delta_{\vec{k}',\vec{k}}\langle \vec{k}, \alpha'|\vec{p}|\vec{k}, \alpha\rangle \; , \qquad (27)$$

$$\langle \vec{k}, \alpha|\vec{p}|\vec{k}, \alpha\rangle \equiv m_0\vec{v}_\alpha(\vec{k}) = (m_0/\hbar)\nabla E_\alpha(\vec{k}) \; , \qquad (28)$$

$$\langle -\vec{k}, \alpha'|\vec{p}|-\vec{k}, \alpha\rangle = -\langle \vec{k}, \alpha'|\vec{p}|\vec{k}, \alpha\rangle^* \; , \qquad (29)$$

where α denotes the band index and $\vec{k}$ is the wave vector. Inserting Eqs. (27)−(29) into Eq. (25) yields the relation

$$\sum_{\alpha\alpha'}\sum_{\vec{k}}|\langle k,\alpha|p_\mu|k\alpha'\rangle|^2 v_{\alpha,\mu}(\vec{k})$$

$$\times F(E_\alpha(\vec{k}),E_{\alpha'}(\vec{k})) \; , \qquad (30)$$

which is zero because of the general relations

$$E_\alpha(-\vec{k})=E_\alpha(\vec{k}), \quad \vec{v}_\alpha(-\vec{k})=-\vec{v}_\alpha(\vec{k}) \; , \qquad (31)$$

which stem from time-reversal symmetry.[24] The function F solely depends on energy.

(iii) A simple system which shows an ABPVE is a system of polarized impurities having a bound state $|0\rangle$. In this case, the transition probabilities to delocalized states $|\vec{k}\rangle$ are expected to be different for $\vec{k}$ and $-\vec{k}$, respectively. Hence, there is no symmetry relation like Eq. (29) which causes Eq. (30) to be zero.

(iv) In an approximation which takes into account three or more bands of the complete set of Bloch states in a pure polar crystal, j_{sc} may become nonzero. At first glance, this is a rather unexpected result because Belinicher et al.[9] and Heyszenau[11] claimed that there is no ABPVE for pure Bloch states.

In a three-band case, the ABPVE arises as a consequence of interfering amplitudes for optical excitation and relaxation processes. We suppose that overlapping conduction bands should be very efficient for this mechanism. Obviously, such interference effects lie outside the scope of the Glass model.

(v) Another interesting aspect of our theory is the fact that the existence of an excited impurity state $|1\rangle$ with low binding energy $|E_1| \simeq \hbar/\tau$, may considerably influence the spectral dependence of $j_{sc}(\omega)$ and can even cause sign changes near the absorption edge, cf Ref. 8. Again, this phenomenon is due to an interference effect. There are two different transition amplitudes for the electron in the ground state $|0\rangle$ to reach delocalized states $|k\rangle$: a direct transition from $|0\rangle$ to $|k\rangle$, and a transition from $|0\rangle$ to $|1\rangle$ and sub-

sequently to $|k\rangle$ via the relaxation mechanism. Additionally, the excited level is broadened by relaxation which then overlaps with states in the Urbach tail which originates from damping processes too. We have not yet performed a numerical evaluation of Eq. (25) which is based on the correct band structure of a real ferroelectric. Nevertheless, we conclude from (iv) that in pure BaTiO$_3$ the observed ABPVE might be due to interband transitions. Furthermore, band-stucture calculations for BaTiO$_3$ demonstrate[25] the existence of several overlapping conduction bands whose transition probabilities from valence band states strongly depend on the polarization of the radiation. By using arguments analogous to (v), we speculate that even the complicated spectral dependence of $j_{sc}(\omega)$ for light polarized parallel to the direction of the spontaneous polarization, might be understood by a multiband model with overlapping bands. An alternative mechanism will be discussed in Sec. V.

V. MODEL CALCULATION

As a first application of our theory, we calculate explicitly the SCPVC for an ensemble of identical, independent, parallel oriented, one-dimensional, polarized impurities whose individual potential is represented by

$$V(x) = -V_1\delta(x) - V_2\delta(x - a) \quad . \tag{32}$$

The stationary states and transition matrix elements between the bound state $|0\rangle$ and delocalized states $|k\rangle$ have already been given in Ref. 12. Merely the matrix elements between scattering states remain to be calculated, but this presents no problem.

The parameters of this model will be fixed in such a manner that both the magnitude and the spectral dependence of $j_{sc}(\omega)$ closely resembles experimental

results for KNbO$_3$:Fe and BaTiO$_3$, respectively. The impurity concentration N, the energy E_0 of the bound state, τ, and the dipole moment d of an impurity in its ground state are known from experiment, or at least plausible estimates can be given. These requirements fix the remaining parameters V_1, V_2 and a in Table I. Because Eq. (32) is not related to a charge distribution which contains a net positive charge, we define an "effective" dipole moment according to

$$d = -e\langle o|x|0\rangle + eaV_2/(V_1 + V_2) \quad . \tag{33}$$

The absorption constant $\alpha(\omega)$ is calculated from the dielectric function

$$\epsilon(\omega) = \bar{\epsilon} + (Ne^2/\hbar\epsilon_0) \sum_{n \neq 0} |\langle n|x|0\rangle|^2 [(\omega - \Omega_n)^{-1}$$
$$- (\omega + \Omega_n{}^*)^{-1}] \quad , \tag{34}$$

where $\hbar\Omega_n = E_n - E_0 - i\hbar/\tau$ and $\bar{\epsilon}$ denotes a background dielectric constant.

For BaTiO$_3$ possible candidates for states $|0\rangle$ and $|1\rangle$ have been observed by Wemple[27] and Berglund and Braun,[28] respectively: E_0 may be related to a localized state just above the valence band and E_1 lies 0,2 eV below the conduction-band edge. The concentration of these impurities has been adjusted to 2.5×10^{20} in order to reproduce the measured additional absorption given in Ref. 27. Possibly, states $|0\rangle$ and $|1\rangle$ may be also related to intrinsic localized states in the valence and conduction band tails.

The numerical results of our calculations are summarized in Figs. 2–4. It is rather puzzling that set (b) fits perfectly in the complicated spectral dependence of $j_{sc}(\omega)$ which has been observed in BaTiO$_3$ for light polarized parallel to the direction of spontaneous polarization. Of course, nothing can be said

TABLE I. Parameters which were used in our model calculation. Experimental results or estimates are given in parenthesis. For LiNbO$_3$ we have a similar situation but $V_2 \ll V_1$.

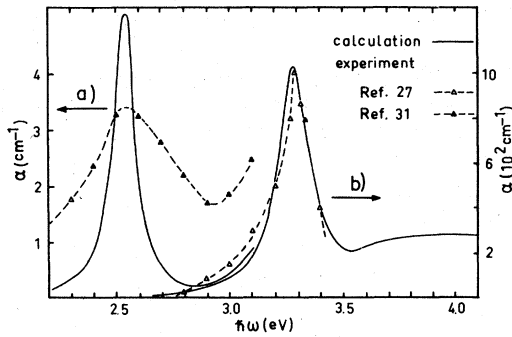| parameter	(a) "KNbO$_3$-like"	(b) "BaTiO$_3$-like"
E_0 (eV)	−3.0 ($\leq$ −3.0, Ref. 31)	−3.5 eV (see text)
E_1 (eV)	−0.47 ($|E_0 - E_1| \approx 2.55$, Ref. 31)	−0.2 eV (see text)
N (cm^{-3})	2×10^{18} ($\approx$Fe^{2+} conc., Ref. 31)	2.5×10^{20} (see text)
d (e Å)	1.1 ($\approx$ dipole moment of unit cell)	0.7 ($\approx$ dipole moment of unit cell)
τ (sec)	1.3×10^{-14} (2×10^{-14}, Ref. 8)	0.7×10^{-14} (10^{-14}, Ref. 29)
$\bar{\epsilon}$	5.9 Ref. 26	5.5 Ref. 30
V_1 (eV Å)	2.6	3.0
V_2 (eV Å)	6.7	7.1
a (Å)	3.5	2.5

FIG. 2. Spectral dependence of the absorption constant for both sets of parameters (a) and (b), respectively.

for perpendicular polarization. For $KNbO_3$:Fe the experimental absorption spectrum is broader than our theoretical result for parameter set (a). This is probably due to a spectral distribution of excited Fe^{2+} states which is intrinsically broader than $\hbar/\tau$. By the same reason the experimental SCPVC spectrum does not exhibit the fine structure that the calculated spectrum shows.

Of course, we know that the electronic structure of a real ferroelectric is much more complicated than that of our model and we know that there are profound arguments against overemphasizing the results of such a calculation. Nevertheless, many other people, e.g., Refs. 33 and 34, have successfully used potentials of this kind for a simple and qualitative description even for rather complicated systems.
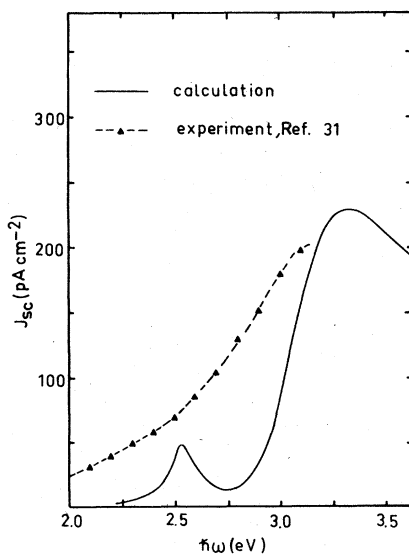

FIG. 3. Spectral dependence of the SCPVC density for parameter set (a) ("$KNbO_3$-like"). $I_0 = 1$ W/cm^2.
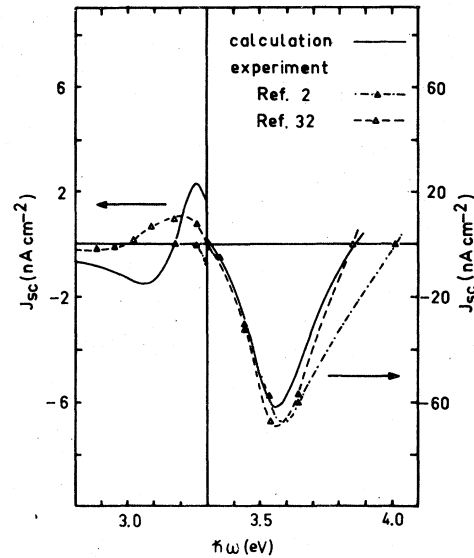

FIG. 4. Spectral dependence of the SCPVC density for parameter set (b) ("BaTiO$_3$-like"). Notice the change of scale factors for $j_{sc}(\omega)$ at 3.3 eV and that we plot the current density $j \approx J\alpha/w$, whereas Koch et al.[2] and Jösch[32] specify the total current J. $w \approx 2$ mm denotes the width of the crystal. $I_0 = 1$ W/cm^2.

VI. SUMMARY AND CONCLUSIONS

In this paper, we present a phenomenological description of the ABPVE and an exact formula for the SCPVC in terms of the quantum states of the system. This theory does not a priori assume a two-step separation of optical excitation and subsequent diffusion processes, as is postulated in the Glass model. Our theory leads to an ABPVE, even in a system of pure Bloch states with assistance of a damping mechanism. Numerical results of a simple model-calculation demonstrate that sign changes in the SCPVC are intimately connected with quantum-mechanical interference phenomena. Additionally, we draw attention to the possibility that the impurity state in $BaTiO_3$ just above the valence band edge may be responsible for the ABPVE. In conclusion, the three-band mechanism mentioned in Sec. IV and the impurity-model in Sec. V offer two independent mechanisms for the ABPVE in $BaTiO^3$. We doubt that the Frank-Condon relaxation mechanism proposed by Chanussot and Glass[14] alone would be able to describe sign changes of the SCPVC.

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