Broken symmetry of the kinetic coefficients and specular polarization phenomena

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The optical consequences of the violation of thermodynamic equilibrium in a crystal are investigated. If this violation occurs it may lead to breaking of time reversibility. As a result of this the internal symmetry of the optical susceptibility tensors changes and new "forbidden" tensor components arise. This gives way to some forbidden specular polarization phenomena in optics, observation of which may be used for diagnostics of the crystal equilibrium. The wave theory of normal reflection from a crystal interface including consideration of the role of the forbidden components is developed. Two mechanisms for forbidden specular polarization effects are identified, one due to the appearance of a contribution to the dielectric tensor which is antisymmetric under interchange of tensor indices, and another associated with the symmetric contribution to the nonlocal optical response. Crystal point group analysis shows that, depending on crystal class, forbidden specular polarization effects may be seen with or without a background of "conventional" optical activity. The physical conditions for their observation are discussed and recent polarization-sensitive experiments in optically excited GaAs crystals are explained in terms of the developed theory. It is also shown how this approach may be used for the description of time-reversal-symmetry-breaking specular optical activity in the superconducting phase of high-T_c cuprate materials.

I. INTRODUCTION

Optical polarization-sensitive detection has already been recognized as a unique and direct tool for the analysis of symmetry-breaking phenomena in physics. For example, breaking of the CPT-invariance resulting from the weak interaction of an optical electron with a nucleus manifests itself as a very small ($\approx 10^{-8}$ rad) rotation of the plane of polarization of a light beam resonantly interacting with the atomic vapor.[1] Specular polarization-sensitive experiments were suggested as a crucial test for the "anyon" superconductivity model, predicting the breaking of time-reversal and possibly parity invariance in cuprate materials.[2–4] An optical test based on polarization-sensitive spectroscopy was suggested and undertaken to search for broken time-reversal invariance in atoms leading to the appearance of permanent electric dipole momentum in the ground state of an alkali atom.[5] It was also found that polarization-sensitive detection may be used in the observation of light-induced symmetry breaking in nonlinear optical resonators, anisotropic crystals and fibers, optically active liquids, and various other nonlinear systems where an intensive electromagnetic wave may provoke violation of a system's spatial symmetry.[6]

In this paper we will show how a polarization-sensitive detection technique may be used for analysis of the breaking of time-reversal symmetry resulting from the loss of thermodynamic equilibrium in a system. The fact that the system, interacting with external forces, meets time-reversibility requirements, leads to some additional internal symmetry arising from the so-called principle of the symmetry of kinetic coefficients (SKC principle), which itself results from the fluctuation-dissipation theorem.[7,8] The interaction of a light wave with matter may be considered as an example of such a system, where the presence of this internal symmetry may be formulated in terms of optical susceptibilities. Loss of the thermodynamic equilibrium of the system may lead to breaking of time reversibility and to the appearance of normally forbidden components of the susceptibility tensors which may be identified by specular polarization-sensitive detection experiments. Below we will show which particular symmetry requirements arise from the SKC principle,[9] how this is reflected in the optical susceptibilities, and how the lifting of thermodynamic equilibrium may be detected by polarization-sensitive detection.

II. THE PRINCIPLE OF THE SYMMETRY OF THE KINETIC COEFFICIENTS

Let us consider a system affected by N external forces $f_s(t)$ $(s=1,2,\ldots,N)$. Energy variation resulting from this excitation may be presented in the form

$$V=x_s f_s(t)\ , \tag{1}$$

where x_s are the internal coordinates corresponding to the external forces $f_s(t)$. The general form of the linear solutions to the corresponding dynamic problem in spectral presentation has the following structure: $x_s(\omega)=\alpha_{sp}(\omega)f_p(\omega)$. The so-called kinetic coefficients, $\alpha_{sp}(\omega)$ $(s,p=1,2,\ldots,N)$ should obey the following relationship: $\alpha_{sp}(\omega)=\pm\alpha_{ps}(\omega)$. Here, the $+$ sign is appropriate if both the force $f_s(\omega)$ and the corresponding coordinate $x_s(\omega)$ have the same symmetry with respect to time inversion $(t\Longrightarrow -t)$, and the $-$ sign if they have opposite symmetry. This is the SKC principle.[8]

In order to apply this concept to optics we adopt the following light-molecule interaction Hamiltonian:[7]

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$$V=-\mathbf{d}\cdot\mathbf{E}-\mathbf{m}\cdot\mathbf{B}-Q_{ij}\nabla_j E_i \ . \tag{2}$$

Here $\mathbf{d}$, $\mathbf{m}$, and Q_{ij} are respectively the electric dipole, magnetic dipole, and quadrupole momenta of the molecule. The last two terms here are essential in the consideration of spatial dispersion effects such as optical activity which will be of special interest below. Below we will consider only nonmagnetic material presuming the absence of any external magnetic fields except the fields of the light wave. In such a case the electric dipole and quadrupole momenta are even functions of time, i.e., $\mathbf{d}(t)=\mathbf{d}(-t)$ and $Q_{ij}(t)=Q_{ij}(-t)$, while the magnetic moment is an odd function: $\mathbf{m}(t)=-\mathbf{m}(-t)$.[10]

From (1) and (2) we can see that, with respect to the SKC principle, the Cartesian projections of the electric field strength E_i, of the magnetic induction B_i, and of the derivative $\nabla_l E_i$ act in optics with respect to the material system as the external excitation forces, while the Cartesian projections of the electric, magnetic, and the quadrupole momenta play the role of the internal coordinates of the molecule:

$$d_i(\omega)=\chi^{(1)}_{ij}(\omega)E_j(\omega)+\alpha_{ij}(\omega)B_j(\omega)+\phi_{ijl}(\omega)\nabla_l E_j(\omega) \ , \tag{3}$$

$$m_i(\omega)=\beta_{ij}(\omega)E_j(\omega)+\mu_{ij}(\omega)B_j(\omega)+\phi^{(m)}_{ijl}(\omega)\nabla_l E_j(\omega) \ , \tag{4}$$

$$Q_{il}(\omega)=\psi_{ilj}(\omega)E_j(\omega)+\psi^{(m)}_{ilj}(\omega)B_j+\kappa_{iljm}(\omega)\nabla_m E_j(\omega) \ . \tag{5}$$

Correspondingly the parameters $\chi^{(1)}_{ij}$, α_{ij}, ϕ_{ijl}, β_{ij}, μ_{ij}, $\phi^{(m)}_{ijl}$, ψ_{ilj}, $\psi^{(m)}_{ilj}$, κ_{iljm} are kinetic coefficients which, in accordance with the SKC principle, must obey the following relations:

$$\begin{aligned}
&\chi^{(1)}_{ij}(\omega)=\chi^{(1)}_{ji}(\omega) \ , \quad \mu_{ij}(\omega)=\mu_{ji}(\omega) \ , \\
&\phi_{ijl}(\omega)=\phi_{jil}(\omega) \ , \quad \psi_{ijl}(\omega)=\psi_{jil}(\omega) \ , \\
&\kappa_{iljm}(\omega)=\kappa_{jmil}(\omega) \ , \quad \phi_{ijl}(\omega)=-\psi_{jil}(\omega) \ , \\
&\alpha_{ij}(\omega)=-\beta_{ji}(\omega) \ , \quad \phi^{(m)}_{ijl}(\omega)=-\psi^{(m)}_{jil}(\omega) \ .
\end{aligned} \tag{6}$$

Here, the different time-reversal symmetry of the forces is taken into account according to the rules stated above.

Considering a wave propagation problem we shall find how (6) affects the current density, $\mathbf{J}(\omega)$, induced by an electromagnetic wave of frequency ω:

$$J_i(\omega)=i\omega d_i+ce_{ilj}\nabla_l m_j(\omega)-i\omega\nabla_l Q^{il}(\omega) \ , \tag{7}$$

where c is the speed of light. Using (3)–(5) we can rearrange the equation above:

$$\begin{aligned}
J_i(\omega)=&i\omega\chi^{(1)}_{ij}(\omega)E_j(\omega)+i\omega\alpha_{ij}(\omega)B_j(\omega)+ce_{ilj}\beta_{jk}(\omega)\nabla_l E_k(\omega)+i\omega[\phi_{ijl}(\omega)-\psi_{ilj}(\omega)]\nabla_l E_j(\omega) \\
&+ce_{ilj}\nabla_l[\mu_{jk}(\omega)B_k(\omega)+\phi^{(m)}_{jkm}(\omega)\nabla_m E_k(\omega)]+i\omega\nabla_l[\psi^{(m)}_{ilj}(\omega)B_j(\omega)+\kappa_{iljm}(\omega)\nabla_m E_j(\omega)] \ .
\end{aligned} \tag{8}$$

The last two contributions, i.e., those which are proportional to ∇B and $\nabla\nabla E$, are in fact related to second-order spatial dispersion phenomena which may be ignored at this stage if attention is concentrated on the phenomenon of optical activity. From the Maxwell equation $B_i(\omega)=i(c/\omega)e_{ilj}\nabla_l E_j(\omega)$, we finally get the current density in a form suitable for the treatment of propagation phenomena in homogeneous materials:

$$J_i(\omega)=i\omega[\chi^{(1)}_{ij}(\omega)E_j(\omega)+\sigma^{(1)}_{ijl}(\omega)\nabla_l E_j(\omega)] \ , \tag{9}$$

where

$$\sigma^{(1)}_{ijl}(\omega)=\phi_{ijl}(\omega)-\psi_{ilj}(\omega)+i\frac{c}{\omega}[\alpha_{ik}e_{klj}+\beta_{kj}e_{kli}] \ . \tag{10}$$

If (6) is introduced into (1), one can see that the application of the SKC principle to nonlocal optics results in

$$\sigma^{(1)}_{ijl}(\omega)=-\sigma^{(1)}_{jil}(\omega) \ . \tag{11}$$

More often in optics, instead of using the material equation (9), a treatment based on the electric induction $\mathbf{D}$ is used:

$$\mathbf{D}(\mathbf{r},t)=\mathbf{E}(\mathbf{r},t)+4\pi\int_{-\infty}^{t}dt'\mathbf{J}(\mathbf{r},t') \ , \tag{12}$$

and correspondingly the following material equation in homogeneous materials is exploited:

$$D_j(\omega)=\epsilon_{ij}(\omega)E_j(\omega)+\gamma_{ijl}(\omega)\nabla_l E_j(\omega) \ , \tag{13}$$

where $\epsilon_{ij}(\omega)=\delta_{ij}+4\pi\chi^{(1)}_{ij}(\omega)$, $\gamma_{ijl}(\omega)=4\pi\sigma_{ijl}(\omega)$, and the last term in (13) describes nonlocal phenomena such as optical activity. Consequently from (9) and (11), the tensors describing thermodynamical-equilibrium interactions should obey the following remarkable symmetry relations:

$$\epsilon_{ij}(\omega)=\epsilon_{ji}(\omega) \ , \tag{14}$$

$$\gamma_{ijl}(\omega)=-\gamma_{jil}(\omega) \ . \tag{15}$$

The restrictions above supplement the symmetry restrictions on the ϵ_{ij} and γ_{ijk} tensors appearing from the point group of the crystal that they are destined to describe. The existence of the restrictions (14) and (15) leads to the forbiddance of some optical phenomena and below we will show how they affect specular polarization effects.

Since the SKC principle reflects the fact that successive states of the system are time-reversed conjugate and derives ultimately from the fluctuation-dissipation theorem, it may not hold for nonequilibrium conditions,

TABLE I. Symmetry restrictions, nonvanishing optical susceptibility components, and corresponding optical phenomena. The + sign indicates here the existence of the corresponding symmetry or tensor component, while − means that the symmetry is broken or the component is forbidden.

T	+	+	−	−	Phenomena in transmission	Specular phenomena $\mathrm{Im}\epsilon^s_{xx} \ll \lvert\mathrm{Re}(1-\epsilon^s_{xx})\rvert$	
P	+	−	+	−			
$\mathrm{Re}\epsilon^s_{ij}$	+	+	+	+	Linear birefringence	Elliptization of polarization	
$\mathrm{Im}\epsilon^s_{ij}$					Linear dichroism	n/a	
$\mathrm{Re}\gamma^a_{ijk}$	−	+	−	+	Circular birefringence	Elliptization of polarization	
$\mathrm{Im}\gamma^a_{ijk}$					Circular dichroism	Polarization rotation	
$\mathrm{Re}\epsilon^a_{ij}$	−	−	+	+	Gyrotropic circular birefringence	Polarization rotation	Phenomena forbidden by the SKC principle
$\mathrm{Im}\epsilon^a_{ij}$					Gyrotropic circular dichroism	Elliptization of polarization	
$\mathrm{Re}\gamma^s_{ijk}$	−	−	−	+	Gyrotropic linear birefringence	Elliptization of polarization	
$\mathrm{Im}\gamma^s_{ijk}$					Gyrotropic linear dichroism	Polarization rotation	

say if the system is exposed to a strong transient excitation or is undergoing a phase transition. In such circumstances, the relationships (14) and (15) may be broken and the dielectric tensor ϵ_{ij} and the optical nonlocality tensor γ_{ijl} may have nonvanishing antisymmetric, $\epsilon^a_{ij}=-\epsilon^a_{ji}$, and symmetric, $\gamma^s_{ijl}=\gamma^s_{jil}$, components, respectively.

As stated above, violation of the SKC principle appears when external forces lead to a response with time-reversal symmetry different from the symmetry of an equilibrium response. In this sense the violation of the SKC principle may be seen as a violation of the time-reversal symmetry (T symmetry). However, Neumann's principle still remains valid here and in calculating nonvanishing tensor components one should take into account also the crystal's whole point group symmetry. However, the presence or absence of P symmetry (space-reversal symmetry) as an element of the point group is the most important factor since the existence of an inversion center in a crystal leads to the forbiddance of any odd-rank material tensor, including the nonlocality tensor γ_{ijk}.

Correspondingly, Table I presents the allowed nonvanishing components which may appear under basic types of symmetry restrictions.

III. MATERIAL EQUATION AND BOUNDARY CONDITIONS IN THE PROBLEM OF REFLECTION

Now we are in a position to consider the role of these "forbidden" tensor components in the specular optical activity phenomenon. We will develop further the approach first used by Bokut' and Serdukov[11] and recently extended towards absorbing media in our publication.[12] In order to consider the interface between a vacuum and an optically nonlocal medium we shall first of all improve the material equation describing homogeneous media (13), making it suitable for the boundary problem, where dramatic variation of material parameters at the interface must be described. We shall start from the general form of the material equation which takes into account the response nonlocality and the causality principle:[9,12]

$$D_i(\mathbf{r},t)=\int d\boldsymbol{\rho}\int_0^\infty d\tau\,\epsilon^{(1)}_{ij}(\boldsymbol{\rho},\mathbf{r}-\boldsymbol{\rho},\tau)E_j(\mathbf{r}-\boldsymbol{\rho},t-\tau)\ , \tag{16}$$

where $\epsilon^{(1)}_{ij}$ is the linear optical response function. The time-domain Fourier transformation of (16) results in

$$D_i(\mathbf{r},\omega)=\int d\boldsymbol{\rho}\,\epsilon^{(1)}_{ij}(\boldsymbol{\rho},\mathbf{r}-\boldsymbol{\rho},\omega)E_j(\mathbf{r}-\boldsymbol{\rho},\omega)\ , \tag{17}$$

where

$$\epsilon^{(1)}_{ij}(\boldsymbol{\rho},\mathbf{r}-\boldsymbol{\rho},\omega)=\frac{1}{2\pi}\int_0^\infty d\tau\,\epsilon^{(1)}_{ij}(\boldsymbol{\rho},\mathbf{r}-\boldsymbol{\rho},\tau)\exp(i\omega\tau)\ . \tag{18}$$

The electromagnetic wave $E_i(\mathbf{r}-\boldsymbol{\rho},\omega)$ and the optical response function may now be expanded to consider the first-order spatial dispersion effects only:

$$E_i(\mathbf{r}-\boldsymbol{\rho},\omega)=E_i(\mathbf{r},\omega)-\rho_l[\partial E_i(\mathbf{r},\omega)/\partial r_l]+\cdots\ , \tag{19}$$

$$\epsilon^{(1)}_{ij}(\boldsymbol{\rho},\mathbf{r}-\boldsymbol{\rho},\omega)=\epsilon^{(1)}_{ij}(\boldsymbol{\rho},\mathbf{r},\omega) -\rho_l[\partial\epsilon^{(1)}_{ij}(\boldsymbol{\rho},\mathbf{r},\omega)/\partial r_l]+\cdots\ . \tag{20}$$

If we now introduce

$$\epsilon_{ij}(\mathbf{r},\omega)=\int d\boldsymbol{\rho}\,\epsilon^{(1)}_{ij}(\boldsymbol{\rho},\mathbf{r},\omega)\ ,\qquad \gamma_{ijl}(\mathbf{r},\omega)=\int d\boldsymbol{\rho}\,\rho_l\epsilon^{(1)}_{ij}(\boldsymbol{\rho},\mathbf{r},\omega) \tag{21}$$

and substitute (19) and (20) into (17), we finally get the material equation in a form more precise than (13):

$$D_i(\mathbf{r},\omega)=\epsilon_{ij}(\mathbf{r},\omega)E_j(\mathbf{r},\omega)+\nabla_l[\gamma_{ijl}(\mathbf{r},\omega)E_j(\mathbf{r},\omega)]\ . \tag{22}$$

The last term here may be rearranged:

$$\nabla_l[\gamma_{ijl}(\mathbf{r},\omega)E_j(\mathbf{r},\omega)]$$
$$=[\nabla_l\gamma_{ijl}(\mathbf{r},\omega)]E_j(\mathbf{r},\omega)+\gamma_{ijl}(\mathbf{r},\omega)[\nabla_l E_j(\mathbf{r},\omega)] \ . \quad (23)$$

In order to describe propagation phenomena such as natural optical activity we can neglect the first part in the right-hand side of (23). This results in the material equation (13). The above simplification is acceptable only when the characteristic length of the variation of $\gamma_{ijl}(\mathbf{r},\omega)$ is sufficiently longer than the light wavelength λ, $|\nabla\gamma(\mathbf{r},\omega)| \ll |\gamma(\mathbf{r},\omega)/\lambda|$ and therefore not acceptable in the theory of reflection. We will be keeping this term in our treatment below. However, this additional term does not affect the time-reversal properties of the optical response of the medium.

In order to proceed with the consideration of specular optical activity, we shall, for simplicity, assume steplike behavior of ϵ_{ij} and γ_{ijl} near the interface plane which corresponds to $z=0$. That is $\epsilon_{ij}=\delta_{ij}$ and $\gamma_{ijl}=0$ at $z<0$ and $\epsilon_{ij}\neq\delta_{ij}$ and $\gamma_{ijl}\neq 0$ at $z>0$ where δ_{ij} is the Kronecker delta symbol. From the Maxwell equation $\nabla\times\mathbf{B}=(1/c)\partial\mathbf{D}/\partial t$, following Ref. 13, by integration over the area of a loop enclosing the border we get the boundary condition for the magnetic induction of the light wave:

$$[\mathbf{n}\times(\mathbf{B}^{(1)}-\mathbf{B}^{(2)})]_i=\frac{1}{c}\frac{\partial}{\partial t}\gamma^{(2)}_{ijz}E^{(2)}_j \ , \quad (24)$$

where $\mathbf{n}$ is the unit vector normal to the interface and the indices (1) and (2) label the vacuum and gyrotropic medium, respectively. The right-hand side of this boundary condition is associated with the induced surface current leading to the effect of specular optical activity. It arises only if the term $(\nabla_l\gamma_{ijl})E_j$, in (23) is taken into consideration. Similarly from the Maxwell equation $\nabla\times\mathbf{E}=-(1/c)\partial\mathbf{B}/\partial t$ the second boundary condition for the electric field may be derived:

$$[\mathbf{n}\times(\mathbf{E}^{(1)}-\mathbf{E}^{(2)})]=0 \ . \quad (25)$$

IV. "FORBIDDEN" SPECULAR POLARIZATION PHENOMENA

From this point we will consider two specific cases of specular polarization phenomena, clearly reflecting the roles of the "forbidden" components of the material tensors ϵ^a_{ij} and γ^s_{ijk}. We will examine reflection of light along the direction of the optic axis of uniaxial crystals or the fourth-order symmetry axis of a cubic crystal and consequently only relevant tensor components will be taken into consideration. For the tensors ϵ_{ij} and γ_{ijk} these are only components with $i,j=x$ or y, and $k=z$. We shall point out here that optical phenomena "in transmission" due to ϵ^a_{ij} and γ^s_{ijk} are known in magnetic materials[14,15] as gyrotropic circular and linear birefringence "in transmission" (see Table I and Ref. [14]). As we have mentioned above, here we consider specular phenomena only in nonmagnetic materials.

First, the crystal classes where ϵ^a_{ij} is not allowed by the crystal point group, but γ_{ijz} (either symmetric or antisymmetric part) is permitted, will be considered. These are 32, $3m$, 422, 622, $4mm$, $\bar{4}2m$, $6mm$, $\bar{4}3m$, 23, 432. From the crystals in this list γ^s_{ijz} is allowed by the point group only in the following classes: $3m$, $4mm$, $\bar{4}2m$, $6mm$, $\bar{4}3m$, 23 while γ^a_{ijz} may be found in 32, 422, 622, 23, 432. We mention here that it is only possible for both symmetric and antisymmetric parts of the nonlocality tensor to exist in the 23 crystal point group.

Second, the case where ϵ^a_{ij} is allowed by the crystal point group will be considered. We will show that even in the direction of the optic axis of a birefringent crystal the existence of ϵ^a_{ij} leads to specular polarization effects. This may happen in the following crystal classes: 3, $\bar{3}$, $\bar{4}$, 4, $4/m$, 6, $\bar{6}$, $6/m$. Correspondingly higher-order contributions to the optical response coming from the nonlocality tensor γ_{ijz} may be ignored here in first approximation.

A. Specular polarization effects in 32, $3m$, 422, 622, $4mm$, $\bar{4}2m$, $6mm$, $\bar{4}3m$, 23, 432 classes due to circular and gyrotropic linear birefringence and dichroism

We introduce the Cartesian coordinate frame where the light beam propagates and reflects along the z direction and the reflecting x-y plane $\langle 001\rangle$ is the surface of the crystal, acting as a mirror, i.e., the normal incidence condition is considered. The electric field in a vacuum $\mathbf{E}^{(1)}$ is given by

$$\mathbf{E}^{(1)}=\mathbf{E}_i\exp(-i\omega t+ikz)+\mathbf{E}_r\exp(-i\omega t-ikz)+\text{c.c.} \ , \quad (26)$$

where $\mathbf{E}_i$ and $\mathbf{E}_r$ are the magnitudes of the incident and the reflected waves and $k=\omega/c$. The wave equations for the Cartesian components of the transmitted wave $\mathbf{E}^{(2)}$ are

$$E_x''+k^2(\epsilon E_x+\gamma_{xxz}E_x'+\gamma_{xyz}E_y')=0 \ , \quad (27)$$

$$E_y''+k^2(\epsilon E_y+\gamma_{yyz}E_y'+\gamma_{yxz}E_x')=0 \ . \quad (28)$$

Here the prime sign refers to the derivative over the direction of wave propagation, i.e., z direction. The form of the Eqs. (27) and (28) is suitable for the description of light propagation in a cubic crystal having the dielectric constant ϵ, or along the optic axis of a uniaxial crystal with $\epsilon_{xx}=\epsilon_{yy}=\epsilon$. We define here the parameters $\nu_{s,a}=\frac{1}{4}k[\gamma_{xyz}\pm\gamma_{yxz}]$ and $\nu_{\pm}=\frac{1}{2}k[\gamma_{xxz}\pm\gamma_{yyz}]$ which determine corrections to the dielectric constant caused by the symmetric and the antisymmetric parts of the nonlocality tensor, respectively. The eigenvectors $q_{1,2}=kn_{1,2}$ and the corresponding eigen polarization states $\mathbf{e}_{1,2}$ of the light wave propagating through the medium may now be found from (27) and (28):

$$n_{1,2}=\sqrt{\epsilon+(i\nu_+\pm\nu)^2}+(i\nu_+\pm\nu) \ , \quad (29)$$

$$e_{x1,2}=\frac{\nu_a+\nu_s}{\sqrt{|\nu_-\pm i\nu|^2+|\nu_a+\nu_s|^2}} \ , \quad (30)$$

$$e_{y1,2}=\frac{-\nu_-\mp i\nu}{\sqrt{|\nu_-\pm i\nu|^2+|\nu_a+\nu_s|^2}} \ , \quad (31)$$

where

$$\nu=\sqrt{\nu_a^2-\nu_s^2-\nu_-^2} \tag{32}$$

and the reflected, transmitted, and incident waves are

$$\mathbf{E}_{i,r}=\mathbf{e}_1 A_{i,r1}+\mathbf{e}_2 A_{i,r2} , \tag{33}$$

$$\mathbf{E}^{(2)}=\mathbf{e}_1 A_{t1}\exp(-i\omega t+iq_1 z) + \mathbf{e}_2 A_{t2}\exp(-i\omega t+iq_2 z)+\text{c.c.} \tag{34}$$

Note here that if $\nu_+=\nu_-=\nu_s=0$ and $\nu_a\neq 0$, the eigenwaves are right- and left-circularly polarized as in the simple case of optically active isotropic media. If $\nu_+=\nu_-=\nu_a=0$ and $\nu_s\neq 0$, the eigenwaves are linearly polarized. In the general case the eigenwaves are elliptical. Correspondingly, if $\nu_+=\nu_-=0$, γ^a_{ijz} leads to circular birefringence and circular dichroism in transmission, while γ^s_{ijz} causes gyrotropic linear birefringence and dichroism (see Table I, where we partially adopted the terminology of Ref. [14] and extended for absorbing media).

The boundary conditions (24) and (25) may now be rewritten in terms of the magnitudes of the eigenwaves $A_{1,2}$:

$$A_{i1,2}+A_{r1,2}=A_{t1,2} , \tag{35}$$

$$A_{i1,2}-A_{r1,2}=\xi_{1,2}A_{t1,2} , \tag{36}$$

where

$$\xi_{1,2}=n_{1,2}-2(i\nu_+\pm\nu) . \tag{37}$$

Thus, from (35) and (36) the magnitudes of the reflected waves are equal to

$$A_{r1,2}=\frac{1-\xi_{1,2}}{1+\xi_{1,2}}A_{i1,2} \tag{38}$$

representing the normal incidence Fresnel law where no assumption concerning the validity of the SKC principle is made. Now the polarization state of the reflected wave may be presented in terms of the ellipticity angle $\eta=(\frac{1}{2})\sin^{-1}(s_3/s_0)$ and the angle of rotation of the polarization azimuth $\alpha=(\frac{1}{2})\tan^{-1}(s_2/s_1)$, where s_m $(m=0,\ldots,3)$ are the Stokes parameters: $s_0=E_xE_x^*+E_yE_y^*$, $s_1=E_xE_x^*-E_yE_y^*$, $s_2=2\,\mathrm{Re}(E_xE_y^*)$, $s_3=2\,\mathrm{Im}(E_xE_y^*)$.

The most clear specular polarization effect may be seen when the incident wave is linearly polarized ($\eta_i=0$). If $|\epsilon|\gg|\nu_+\pm i\nu|$:

$$\frac{S_{2r}}{S_{1r}}=\tan 2\phi+\frac{4\,\mathrm{Im}\left[\dfrac{\nu_a-\nu_s\cos(2\phi)+\nu_-\sin(2\phi)}{1-\epsilon}\right]}{\cos^2 2\phi} , \tag{39}$$

$$\frac{S_{2r}}{S_{1r}}=4\,\mathrm{Re}\left[\frac{\nu_a-\nu_s\cos(2\phi)+\nu_-\sin(2\phi)}{1-\epsilon}\right] . \tag{40}$$

Correspondingly, if the polarization change of the reflected waves is small ($\eta_r\ll\pi$, $\delta\alpha_r\ll\pi$) and this is certainly the case for the most experimental situations,

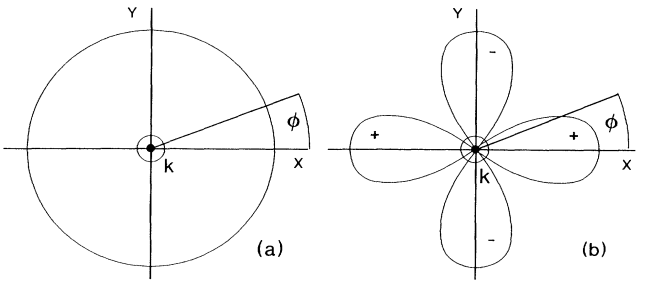

FIG. 1. Specular polarization phenomena in a polar coordinate system. The wave vector of the reflected light is directed towards the observer. (a) Polarization azimuth rotation due to gyrotropic birefringence ($\mathrm{Re}\epsilon^a_{ij}\neq 0$) and circular birefringence ($\mathrm{Re}\gamma^a_{ijz}\neq 0$). (b) The simplest case of gyrotropic linear birefringence (only $\mathrm{Re}\gamma^s_{xyz}\neq 0$).

then

$$\left[\frac{\delta\alpha_r}{\eta_r}\right]=4\left[\frac{\mathrm{Im}}{\mathrm{Re}}\right]\left[\frac{\nu_a-\nu_s\cos 2\phi+\nu_-\sin 2\phi}{1-\epsilon}\right] . \tag{41}$$

As a particular case, the formulas (39) and (40) describe the phenomenon of "conventional" specular optical activity along an isotropic direction[12] in crystals of the following classes: 32, 422, 622, 432, where $\gamma^s_{ijz}=0$ because of the point group restrictions, and violation of the SKC principle does not lead to any "forbidden" specular effects. Here $\nu_s=\nu_-=0$ and since cosine and sine contributions are equal to zero, there is no dependence on the initial polarization plane direction [see Fig. 1(a)]. Here in low-absorbing crystals the polarization plane rotation in reflected light is purely proportional to the imaginary part of the nonlocality tensor γ^a_{ijz}.

In crystals of $3m$, $4mm$, $\bar{4}2m$, $6mm$, $\bar{4}3m$, no "conventional" specular optical activity is allowed by the point groups and $\gamma^a_{ijz}=0$ and correspondingly $\nu_a=0$. At the same time when the conditions for violation of the SKC principle are met, the nonzero components of γ^s_{ijz} appear and "forbidden" specular polarization phenomena due to gyrotropic linear birefringence and dichroism are possible. Here the polarization state of the reflected wave dramatically depends on the initial orientation of the polarization plane with respect to the crystal axis [see Fig. 1(b)]. As we have mentioned above, in the 23 point group both "conventional" (circular) and "forbidden" (gyrotropic linear) birefringence and dichroism are possible.

We note here that the brief results on phenomenological consideration of specular polarization effects in magnetic materials obtained in Ref. 15 were partially wrong because of the use of incorrect material equations in which spatial derivatives of third-rank material tensors were ignored [see formula (23) and our publication[12]].

B. Specular polarization effects in crystals of $3, \bar{3}, \bar{4}, 4, 4/m, 6, \bar{6}, 6/m$ classes due to gyrotropic circular birefringence and dichroism

In the classes listed above, violation of the SKC principle may lead to the appearance of an antisymmetric com-

ponent of the dielectric tensor ϵ_{ij}. In this case, there is no need to include the higher-order phenomena related to γ_{ijl} (the nonlocality tensor). The specular polarization effects here may be considered using the same coordinate system as above, i.e., light propagates in the z direction with the surface of the crystal lying in the x-y plane $\langle 001 \rangle$, acting as a mirror. Here we presume that the coordinate frame is set in a way that the dielectric tensor ϵ_{xy} is diagonal if the SKC principle holds.

The electric field in a vacuum, $\mathbf{E}^{(1)}$, is given by Eq. (26), but the wave equations for the Cartesian components of the transmitted wave $\mathbf{E}^{(2)}$ are different:

$$E_x''+k^2(\epsilon E_x+\epsilon_{xy}^a E_y)=0 , \tag{42}$$

$$E_y''+k^2(\epsilon E_y-\epsilon_{xy}^a E_x)=0 . \tag{43}$$

Here $\epsilon_{xy}^a=-\epsilon_{yx}^a$ is the antisymmetric part of the dielectric tensor resulting in the violation of the SKC principle. The eigen polarization states are right- and left-circularly polarized waves, $\mathbf{e}_\pm=e_x\pm ie_y$, the corresponding eigenvectors $q_\pm=kn_\pm$ are equal to

$$n_\pm=\sqrt{\epsilon\mp i\epsilon_{xy}^a} . \tag{44}$$

In accordance with Table I the optical effect due to the difference between n_+ and n_- is referred to as gyrotropic circular birefringence and dichroism. Because we are neglecting the γ_{ijk} contribution here, the right-hand side of the boundary condition (24) becomes zero, which leads to the following form of the Fresnel law for the normal incidence condition:

$$A_{r\pm}=\frac{1-n_\pm}{1+n_\pm}A_{i\pm} . \tag{45}$$

If the incident wave is linearly polarized and $|\epsilon| \gg |\epsilon_{xy}^a|$ (i.e., $\eta_r \ll \pi$, $\delta\alpha_r \ll \pi$), then

$$\begin{bmatrix}\delta\alpha_r\\ \eta_r\end{bmatrix}=\begin{bmatrix}\mathrm{Re}\\ -\mathrm{Im}\end{bmatrix}\left[\frac{\epsilon_{xy}^a}{\sqrt{\epsilon}(1-\epsilon)}\right] . \tag{46}$$

The specular polarization phenomenon described by this formula does not depend on the incident light polarization plane direction with respect to the crystallographic axes [see Fig. 1(a)].

V. DISCUSSION

Table I presents a summary of the effects which may be seen on reflection from a crystal where no reservation concerning validity of the SKC principle is presumed. In a low-absorbing media ($\mathrm{Im}\epsilon^s \ll |\mathrm{Re}\{1-\epsilon\}|$) specular polarization phenomena manifest themselves as reflected light polarization azimuthal rotation ($\mathrm{Re}\epsilon_{ij}^a \neq 0$, $\mathrm{Im}\gamma_{ijz}^s \neq 0$, or $\mathrm{Im}\gamma_{ijz}^a \neq 0$) or elliptization of polarization of incident linearly polarized light ($\mathrm{Im}\epsilon_{ij}^a \neq 0$, $\mathrm{Re}\gamma_{ijz}^s \neq 0$, or $\mathrm{Re}\gamma_{ijz}^a \neq 0$). In an absorbing medium specular polarization azimuth rotation and elliptical polarization should be expected to happen simultaneously.

In fact there is already at least one experimental observation which may be explained in terms of the violation of the SKC principle.[16] Excitation-induced polarization azimuth rotation has been detected on normal reflection from GaAs, belonging to the $\bar{4}3m$ point group. In zinc-blende crystals ($\bar{4}3m$) the third-rank tensor has the following nonzero components $\gamma_{xyz}=\gamma_{zxy}=\gamma_{yzx}=\gamma_{yxz}=\gamma_{zyx}=\gamma_{xzy}$, a result of the symmetry group. "Conventional" optical activity does not exist here, but due to the breakage of the SKC principle γ_{ijz}^s may appear and, consequently, specular polarization effects due to gyrotropic linear dichroism with a $\cos(2\phi)$ dependence on the initial polarization orientation is predicted by (41):

$$\delta\alpha_r=2k\ \mathrm{Im}\left[\frac{\gamma_{xyz}^s}{\epsilon-1}\right]\cos 2\phi . \tag{47}$$

In the experiment in question the crystal was excited by a 60-ps pulse of green ($\lambda=532$ nm) radiation creating a dense electron-hole plasma in the sample. The rotation of polarization of the reflected light was detected in a separate probe light pulse and was in the scale of 10–100 μrad monotonously, increasing with the excitation which was in the range of 10–200 MW/cm^2. The rotation appeared immediately with the excitation and disappeared steadily in 300 ps, after the excitation pulse had gone. The dependence of the induced effect on the initial polarization orientation was measured with good accuracy and was found to be exactly as predicted by the formula (47).

We explain the observed result in the following way.

(a) The nonequilibrium state is created by fast transient excitation and absorption of the energy of the light pulse. The excitation relaxation time is longer than the duration of the pump pulse and the time-reversal symmetry is broken even after the end of the excitation pulse.

(b) The SKC principle forbidden component of the nonlocality tensor γ_{xyz}^s appears as the result of lifting the conditions of the applicability of the SKC principle [see formula (15)]. In accordance with (39)–(41) this leads to the rotation of the polarization azimuth "on reflection" for a delayed probe pulse. The value of the component of the nonlocality tensor corresponding to a specular probe pulse polarization rotation of 2.5×10^{-5} rad may be estimated via formula (47) as $\gamma_{xyz}^s=2\times10^{-9}$ cm^{-1}. Here we point out that if the antisymmetric part of γ_{ijk} had this value, the corresponding optical rotatory power in transmission would be about 90°/mm, which is a quite typical value for gyrotropic crystals such as α-SiO_2, $Bi_{12}SiO_{20}$.[17] For strongly optically active crystals such as TeO_2, α-HgS, or $LiIO_3$,[17] specific rotation in the visible range is typically 500°–300°/mm and the value of γ^a would be about 10^{-8} cm^{-1}, i.e., one order of magnitude higher than the above-mentioned induced component.

(c) It is most likely that the generation of the dense electron-hole plasma, i.e., excitation of the free carriers, is the main reason for breaking the SKC principle in the optical response. Recombination of the carriers results in the observed disappearance of the nonequilibrium state, the symmetric component of the nonlocality tensor, and the specular rotation of the probe beam.

We believe that the above example is the first demonstration of the violation of the SKC principle in optics due to transient excitation but certainly this kind of "forbidden" phenomena may be found in different crystals.

They should be particularly important in media with strongly nonlocal optical response and appropriate crystalline symmetry. The response nonlocality is very pronounced in organic crystals (especially with weakly bound valence electrons), liquid crystals (especially cholesterics), layered materials with a structure period shorter than the wavelength (semiconductor multiple quantum wells would be an evident but far from unique example), excitonic crystals with bound and free excitons, and semiconductors where optical response is due to the electron-hole plasma. Moreover, any system having microscopic spiral structure and consequently strong polarization rotation power shall evidently be attributed as sufficiently nonlocal. It should be mentioned here that a nonlocal, weakly bound optical electron is a very nonlinear object and consequently optical nonlocality may very often be found side by side with pronounced nonlinearity of the media.

The approach developed above may also be used for describing specular optical polarization phenomena in crystals when time-reversal symmetry is broken due to any reason different than the loss of the thermodynamic equilibrium. This turns us to the problem of the controversial discussion on the existence of optical activity on reflection from some high-T_c materials[18–21] where the formulas (41) and (46) may be used for the description of specular rotation from the superconducting phase. In accordance with the "anyon" superconductivity model cuprate high-T_c materials should have simultaneously broken spatial inversion symmetry P and time inversion symmetry T in the superconducting phase (but PT remains a "good" symmetry[4,21]). In the "PT state" in accordance with Table I [$T=(-)$, $P=(-)$], the antisymmetric part of ϵ_{ij} and the symmetric part of γ_{ijk} are allowed and, correspondingly, specular polarization plane rotation and light elliptical polarization may be expected. However, corresponding tensor components should also be allowed by crystalline symmetry. One specific example of where the crystalline symmetry forbids these tensor components in nonmagnetic materials is the $4/mmm$ crystal class, to which the well known high-T_c material $YBa_2Cu_3O_{7-\delta}$ is attributed. Consequently, if magnetic properties are not taken into account, no specular polarization phenomena due to homogeneous bulk contribution, resulting in broken time reversibility may be expected here.

Summarizing, using the nonlocal light-molecule interaction Hamiltonian we have found the limitation on the linear optical susceptibility of nonmagnetic materials resulting from the principle of the symmetry of the kinetic coefficients. We have also developed the theory of specular optical activity in crystals along nonbirefringent directions, taking into account the role of the components of the dielectric and nonlocality tensor, forbidden by the SKC principle. Recent specular polarization-sensitive time-resolved experiments with an optically excited GaAs crystal are explained using the developed theory. We also point out how the above approach may be used for the problem of specular polarization phenomena in the superconducting phase of cuprate materials.

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