Dispersion-free optical activity in non-centrosymmetric metals

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According to the Onsager principle a matrix of kinetic coefficients is symmetric in a system not violating time inversion symmetry. The antisymmetry is possible in systems with broken time inversion symmetry f.i. in systems in external magnetic field. An exception to this rule is presented here. It is shown that in a tetragonal metals with point group $C_{4v}$ not violating time inversion the conductivity tensor is antisymmetric. The corresponding optical properties are considered.

\section{I. INTRODUCTION}

The natural optical activity or natural gyrotropy is well known phenomenon typical for the bodies having no centre of symmetry \textsuperscript{1}. The optical properties of a naturally active body resemble those of the magneto-active media having no time reversal symmetry. In metals, it is more natural to describe optical properties in terms of spacial dispersion of conductivity tensor having the following form:

$$\sigma_{ij}(\omega, q) = \sigma_{ij}(\omega, q) - i \lambda_{ijkl}(\omega)q_k q_l.$$  \hspace{1cm} (1)

where $\lambda_{ijkl}(\omega)$ is an antisymmetric third rank tensor called the tensor of gyrotropy. In metals, it is more natural to describe optical properties in terms of wave vector.

$$\varepsilon_{ij}(\omega, q) = \varepsilon_{ij}(\omega, q) + i \gamma_{ijkl}(\omega)q_l,$$  \hspace{1cm} (2)

where $\gamma_{ijkl}(\omega)$ is an antisymmetric third rank tensor called the tensor of gyrotropy. In metals, it is more natural to describe optical properties in terms of wave vector.

Here, the gyrotropy tensor $\lambda_{ijkl}(\omega)$ is an odd function of frequency. For an isotropic metal without inversion centre it was calculated in the papers \textsuperscript{2,3}.

Unlike the rotation of the polarisation plane in the magnetic field, in naturally polarised substances, the magnitude and sign of rotation are independent of the direction of beam propagation. Therefore, if a linearly polarized light beam passes twice - back and forth - the same path in a naturally active environment, then in the result it will be polarised in the original plane. The difference is that in the magnetic field the gyrotropy tensor depends only on the properties of the medium, whereas in naturally polarised substances it depends also on the wave vector of the field. As result, the natural optical activity exhibits circular dichroism and circular birefringence, but, unlike a media with broken time reversal symmetry, does not reveal the Kerr effect. The latter property has stimulated discussion \textsuperscript{4,7} in relation with an observation \textsuperscript{8} of rotation of light polarisation reflected from the surface of high $T_c$ superconducting compounds.

In the present work, it will be shown that the optical properties of some non-centre-symmetric media are not limited to the listed above properties. Kinetics of a metal without inversion centre is described by four kinematic equations for the diagonal (intra-band) and the off-diagonal (inter-band) elements of matrix distribution function of electrons occupying the states in two bands split by the spin-orbit interaction \textsuperscript{3}. In some 3D media the off-diagonal terms give rise the contribution to electric current not only due to the interband scattering but also in the collision-less regime where the conductivity acquires an antisymmetric part independent from the field wave vector

$$\sigma_{ij} = -\sigma_{ji},$$  \hspace{1cm} (3)

that is unusual property for media having time reversal symmetry.

The paper is organised as follows. First, we describe the electronic states in metals without centre of inversion. Then there will be presented the system of kinetic equations for the matrix distribution function of electrons. Next, we derive antisymmetric conductivity tensor and consider the corresponding optical properties.

\section{II. ELECTRONIC STATES IN NON-CENTROSYMMETRIC METALS}

Spin-orbit interaction of electrons with a non-centrosymmetric crystal lattice lifts spin degeneracy of electron states. Each band filled by twice degenerate electron states splits on two bands filled by the electron states with different momenta at the same energy. Usually scalar electron energy and the Fermi distribution function are given now by the matrices $\hat{\varepsilon} = \varepsilon_{\sigma\sigma'}$, $\hat{n} = n_{\sigma\sigma'}$ in respect of spin indices.

The spectrum of noninteracting electrons in a metal without inversion center is:

$$\hat{\varepsilon}(k) = \varepsilon(k)\hat{\delta} + \gamma(k) \cdot \sigma,$$  \hspace{1cm} (4)

where $\varepsilon(k)$ denotes the spin-independent part of the spectrum, $\hat{\delta}$ is the unit $2 \times 2$ matrix in the spin space, $\sigma = (\sigma_x, \sigma_y, \sigma_z)$ are the Pauli matrices. The second term in Eq. (4) describes the spin-orbit coupling whose form depends on the specific noncentrosymmetric crystal structure. The pseudovector $\gamma(k)$ satisfies $\gamma(-k) = -\gamma(k)$ and $\gamma(g^{-1}k) = \gamma(k)$, where $g$ is any symmetry operation in the point group $G$ of the crystal. The tetragonal point group $G = C_{4v}$, relevant for CePt$_3$Si, LaPt$_3$Si, CeRhSi$_3$ and CeIrSi$_3$, yields the antisymmetric spin-orbit coupling

$$\gamma(k) = \gamma(k_y \hat{x} - k_x \hat{y}) + \gamma_{\parallel} k_x k_y (k_x^2 - k_y^2) \hat{z}.$$  \hspace{1cm} (5)
In the purely two-dimensional case, setting \( \gamma = 0 \) one recovers the Rashba interaction [10] which is often used to describe the effects of the absence of mirror symmetry in semiconductor quantum wells. The case of isotropic spectrum when \( \varepsilon(k) = \frac{k^2}{2m} \) and
\[
\gamma(k) = \gamma k \tag{6}
\]
is compatible with the 3D cubic crystal symmetry. Here \( \gamma \) is a constant.

The eigenvalues and eigenfunctions of the matrix [11] are
\[
\varepsilon_{\pm}(k) = \varepsilon(k) \pm |\gamma(k)|, \tag{7}
\]
\[
\Psi^+_\sigma(k) = C_k \left( \gamma_{kx} + i \gamma_{ky} \right), \tag{8}
\]
\[
\Psi^-_\sigma(k) = C_k \left( -\gamma_{kx} + i \gamma_{ky} \right),
\]
\[
C_k = (2(\gamma_{kx} + 1))^{-1/2}.
\]

These are the components of the unit vector of spin-orbit coupling. The eigen functions obey the orthogonality conditions
\[
\Psi^*_\alpha(k)\Psi^\beta_\sigma(k) = \delta_{\alpha\beta}, \quad \Psi^*_\sigma_\alpha(k)\Psi^\sigma_\beta(k) = \delta_{\sigma_1\sigma_2}. \tag{10}
\]

Here, in all the subsequent formulas there is implied the summation over the repeating spin \( \sigma = \uparrow, \downarrow \) or band \( \alpha = +, -, 0 \) indices.

By application of the operator of time inversion \( \hat{K} = -i\sigma_y K_0 \), where \( K_0 \) is the complex conjugation operator one can see that the state \( \Psi^\alpha_\sigma(k) \) and the state \( \hat{K}_{\alpha\beta}\Psi^\beta_\sigma(k) \) correspond to the same energy \( \varepsilon_{\alpha\beta}(k) = \varepsilon_{\pm}(k) \) in accordance with the Kramers theorem which is valid in a time inversion conserving systems. A more detailed theoretical description of noncentrosymmetric metals in normal and in superconducting state is presented in the paper [11] and the references therein.

There are two Fermi surfaces determined by the equations
\[
\varepsilon_{\pm}(k) = \mu \tag{11}
\]
with different Fermi momenta \( k_{F,\pm} \). In the Rashba 2D model and in the 3D isotropic case they are
\[
k_{F,\pm} = \mp m\gamma + \sqrt{2m\mu + (m\gamma)^2} \tag{12}
\]
and the Fermi velocity has the common value
\[
v_{F,\pm} = \frac{\partial (\varepsilon_{\pm}(k))}{\partial k} |_{k=k_{F,\pm}} = k \sqrt{\frac{2\mu}{m} + \gamma^2}, \tag{13}
\]
here \( \hat{k} \) is the unit vector along momentum \( k \). The equivalence of the Fermi velocities at different Fermi momenta is the particular property of the models with isotropic spin-orbital coupling [10] in 3D case and the Rashba interaction in 2D case.

The matrix of equilibrium electron distribution function is
\[
\hat{n}^0 = \frac{n_+ + n_-}{2} \hat{\delta} + \frac{n_+ - n_-}{2|\gamma|} \gamma \cdot \sigma, \tag{14}
\]
where
\[
n_{\pm} = \frac{1}{\exp \left( \frac{\varepsilon_{\pm} - \mu}{T} \right) + 1} \tag{15}
\]
are the Fermi functions.

### III. KINETIC EQUATION

The distribution matrix time-variation in the \( (k, r) \) space is determined by the quasi-classic kinetic equation that was derived by V.P. Silin [12] and has the following form
\[
\frac{\partial \hat{n}}{\partial t} + \frac{1}{2} \left( \frac{\partial \hat{\varepsilon}}{\partial k} \frac{\partial \hat{n}}{\partial r} + \frac{\partial \hat{n}}{\partial r} \frac{\partial \hat{\varepsilon}}{\partial k} \right) - \frac{1}{2} \left( \frac{\partial \hat{\varepsilon}}{\partial r} \frac{\partial \hat{n}}{\partial k} + \frac{\partial \hat{n}}{\partial k} \frac{\partial \hat{\varepsilon}}{\partial r} \right) - i[\hat{\varepsilon}, \hat{n}] = \hat{I}_{st}, \tag{16}
\]
where \( [\hat{\varepsilon}, \hat{n}] \) is the commutator of \( \hat{\varepsilon} = \hat{\varepsilon}(k, r) \) and \( \hat{n} = \hat{n}(k, r) \). We put \( \hbar = 1 \). The collision integral in the rhs determines the relaxation processes.

An important simplifications take place in the high frequency region \( \omega \gg v_F/\delta, \omega \gg v_F/l = 1/\tau \), where \( \delta \) is the field penetration depth and \( l \) is the mean free path. These conditions in metals are usually realised in infrared frequency region [13]. In this case one can neglect by the collision integral and by the coordinate dependence of distribution function. In presence of time dependent electric field \( E(t) = E_w e^{-i\omega t} \) the linearised kinetic equation [16] is
\[
\frac{\partial \hat{g}}{\partial t} + eE \frac{\partial \hat{n}^0}{\partial k} - i[\hat{\varepsilon}, \hat{g}] = 0, \tag{17}
\]
where \( \hat{g} = \hat{n} - \hat{n}^0 \) is the deviation of distribution function from equilibrium distribution \( \hat{n}^0 \).

It is quite natural to rewrite kinetic equation in the band representation where the energy matrix is diagonal
\[
\hat{\varepsilon} = \begin{pmatrix}
\varepsilon_+ & 0 \\
0 & \varepsilon_-
\end{pmatrix}, \tag{18}
\]
The hermitian matrices of the nonequilibrium distribution functions in band and spin representations are related as
\[
f_{\alpha\beta}(k) = \Psi^*_{\alpha\sigma_1}(k) n_{\sigma_1\sigma_2} \Psi^\beta_{\sigma_2}(k). \tag{19}
\]
In the band representation the equilibrium distribution function \( f_{\alpha\beta}^0(k) \) is the diagonal matrix

\[
f_{\alpha\beta}^0(k) = \Psi_{\sigma_1\sigma_2}^{\alpha*}(k)n_{\sigma_1\sigma_2}^{\beta}(k) = \begin{pmatrix} n_+ & 0 \\ 0 & n_- \end{pmatrix}_{\alpha\beta}.
\] (20)

However, the matrix of derivative of the equilibrium distribution in the band representation is not diagonal and given by the following equation

\[
\Psi_{\sigma_1}^{\alpha*}(k)\frac{\partial n_{\sigma_2}}{\partial k} \Psi_{\sigma_2}^\beta(k) = \frac{\partial f_{\alpha\beta}^0}{\partial k} + [v_{\alpha\gamma}, f_{\gamma\beta}^0],
\] (21)

where \([\ldots, \ldots]\) is the commutator. Substitution Eqs. (25)–(28) to the Eq. (30) gives

\[
v_{\alpha\beta} = \Psi_{\sigma_1}^{\alpha*}(k)\frac{\partial \Psi_{\sigma_2}^\beta}{\partial k}
\] (22)

Hence, the matrix kinetic equation for the frequency dependent Fourier amplitudes of non-equilibrium part of distribution function \( g_{\alpha\beta}(k, t) = g_{\alpha\beta}(k, \omega)e^{-i\omega t} \) acquires the form

\[
\frac{d}{dt}g_{\alpha\beta}(k, t) = \ldots
\]

The solution of Eq.(23) is

\[
g_+ = \frac{e}{i\omega}(v_+E)\frac{\partial n_+}{\partial \xi_+},
\] (25)

\[
g_- = \frac{e}{i\omega}(v_-E)\frac{\partial n_-}{\partial \xi_-},
\] (26)

\[
g_\pm = \frac{e(v_\pm E)(n_+ - n_-)}{i(\omega - \varepsilon_+ + \varepsilon_-)},
\] (27)

\[
g_\mp = \frac{e(v_\pm E)(n_- - n_+)}{i(\omega - \varepsilon_- + \varepsilon_+)}.
\] (28)

The last term in this formula presents the current directed perpendicular to electric field. Thus, the current consists of two parts

\[
j = \sigma_{ij}^a E_j + \sigma_{ij}^a E_j
\] (32)
absence of relaxation due to electron scattering on im-
centrosymmetric media a high frequency electric field in
determined by the symmetric

\[
\sigma^s_{ij} = \frac{e^2}{i\omega} \int \frac{d^3k}{(2\pi)^3} \left[ \frac{v_{i\pm} v_{j\pm}}{\omega^2 - (\varepsilon_+ - \varepsilon_-)^2} \frac{\partial n_+}{\partial \xi^+} + \frac{v_{i\mp} v_{j\mp}}{\omega^2 - (\varepsilon_+ - \varepsilon_-)^2} \frac{\partial n_-}{\partial \xi^-} - 2\omega^2 (n_+ - n_-) (\varepsilon_+ - \varepsilon_-) \text{Re}(v_{i\pm} v_{j\pm}) \right],
\]

and antisymmetric

\[
\sigma^a_{ij} = 2e^2 \int \frac{d^3k}{(2\pi)^3} \left[ \frac{(n_+ - n_-) (\varepsilon_+ - \varepsilon_-)^2}{\omega^2 - (\varepsilon_+ - \varepsilon_-)^2} \text{Im}(v_{i\pm} v_{j\pm}) \right].
\]

In two dimensions the \( z \)-component of vector \( \gamma(k) \) is absent, and \( \text{Im}(v_{i\pm} v_{j\mp}) = 0 \). Hence, in a 2D non-centrosymmetric media a high frequency electric field in absence of relaxation due to electron scattering on impurities does not produce a contribution to the current conductivity. Unlike to the statement made in the paper [9] both contributions to the current are pure reactive and do not give rise a dissipation. The antisymmetric combination of velocities is

\[
\text{Im}(v_{i\pm} v_{j\pm}^*) = \frac{1}{4(\gamma_{kz} + 1)} \left\{ \frac{\partial \hat{\gamma}_{kz}}{\partial k_i} \left[ -\hat{\gamma}_{kz} \left( \frac{\partial \hat{\gamma}_{ky}}{\partial k_j} \right) + \hat{\gamma}_{ky} \left( \frac{\partial \hat{\gamma}_{kz}}{\partial k_j} \right) \right] + \left( \frac{\partial \hat{\gamma}_{kz}}{\partial k_i} \right) \left[ -\hat{\gamma}_{ky} \frac{\partial \hat{\gamma}_{kz}}{\partial k_i} + \hat{\gamma}_{kx} \frac{\partial \hat{\gamma}_{ky}}{\partial k_i} \right] \right\}. \tag{35}
\]

In pure collision-less regime the symmetric part of conductivity is pure imaginary quantity. The collisions give rise the real contribution to conductivity, so, in general

\[
\sigma^s_{ij} = \sigma^s_{ij}^{'} + \text{i} \sigma^s_{ij}^{''}. \tag{37}
\]

The high frequency antisymmetric part of conductivity derived here originates from the off-diagonal terms in the matrix kinetic equation. It must reveal itself also in presence of electron scattering by impurities, phonons etc. In weak scattering regime, when the impurity scattering rate by impurities is smaller than the band splitting due to spin-orbit interaction \( 1/\tau \ll 2\gamma k_F \), the antisymmetric part of conductivity is still real [6] as it is in collision-free regime according to Eq. (33).

V. OPTICAL PROPERTIES

For the electric field directed in the basal plane of tetragonal metal with symmetry \( C_{4v} \) the electric current density has the following form

\[
\mathbf{j} = \frac{e}{4\pi} \frac{\partial \mathbf{E}}{\partial t} + \sigma_{x} \mathbf{E} + \sigma_{a} (\mathbf{E} \times \hat{z}), \tag{38}
\]

where the first term corresponds to the displacement current related to electrons bound at crystal lattice ions. The second one is the conductivity current. The last one is the dispersion-less gyrotropy current derived in the previous section.

Eliminating the magnetic induction, from the Maxwell equations

\[
\text{rot} \mathbf{B} = \frac{4\pi}{c} \mathbf{j}, \tag{39}
\]

\[
\text{rot} \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} \tag{40}
\]

we obtain

\[
\nabla^2 \mathbf{E} = \frac{\varepsilon}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} + \frac{4\pi \sigma_s}{c^2} \frac{\partial \mathbf{E}}{\partial t} + \frac{4\pi \sigma_a}{c^2} \left( \frac{\partial \mathbf{E}}{\partial t} \times \hat{z} \right). \tag{41}
\]
Taking solution for the circularly polarized wave
\[ \mathbf{E} = (\hat{x} \pm i \hat{y}) E_0 e^{i(kr - \omega t)} \]  \hspace{1cm} (42)
we come to the dispersion relation
\[ k^2 = \frac{\epsilon \omega^2}{c^2} + \frac{4\pi i \omega \sigma_s}{\epsilon^2} \mp \frac{4\pi i \omega \sigma_a}{\epsilon^2}. \]  \hspace{1cm} (43)

In neglect the last term the complex index of refraction
\[ N = \frac{ck}{\omega} = n + i\kappa \]  \hspace{1cm} (44)
is expressed through the diagonal part of complex conductivity \( \sigma_s = \sigma_s' + i\sigma_s'' \) by means of the usual relations
\[ n^2 - \kappa^2 = \epsilon - \frac{4\pi \sigma_s''}{\omega}, \quad 2n\kappa = \frac{4\pi \sigma_s'}{\omega}. \]  \hspace{1cm} (45)

The last term in Eq. [43] term leads to the difference in the refraction indices of clock wise and counter clock wise polarised light.
\[ N_\pm = \frac{ck}{\omega} = n + i\kappa + \delta n_\pm + i\delta \kappa_\pm \]

In the first order in respect to \( \sigma_a \) the corrections to refraction index are
\[ \delta n_\pm = \pm \frac{2\pi n \sigma_a}{\omega(n^2 + \kappa^2)}, \]  \hspace{1cm} (46)
\[ \delta \kappa_\pm = \pm \frac{2\pi \kappa \sigma_a}{\omega(n^2 + \kappa^2)}. \]  \hspace{1cm} (47)

Hence, the differences in the real and imaginary parts of the refraction indices of circularly polarised lights with the opposite polarisation are
\[ \Delta n = n_+ - n_- = -\frac{4\pi n \sigma_a}{\omega(n^2 + \kappa^2)}, \]  \hspace{1cm} (48)
\[ \Delta \kappa = \kappa_+ - \kappa_- = \frac{4\pi \kappa \sigma_a}{\omega(n^2 + \kappa^2)}. \]  \hspace{1cm} (49)

The ratio of the amplitude of the normally incident electric field \( E^i \) to the reflected field \( E^r \) is related to the complex index of refraction according to
\[ R_\pm = \frac{E^r_\pm}{E^i_\pm} = \frac{1 - N_\pm}{1 + N_\pm}. \]  \hspace{1cm} (50)

VI. CONCLUSION

We have demonstrated that high frequency conductivity tensor in tetragonal non-centrosymmetric metals with point group \( \text{C}_4v \) not violating time reversal symmetry is antisymmetric. This property determined by the off-diagonal terms in the matrix kinetic equation for electron distribution function. Unlike the usual natural optic activity giving rise the linear in the field wave vector antisymmetric terms in permeability the derived antisymmetric conductivity is dispersion-free quantity. As the result a linearly polarised light beam normally incident on the basal plane of such a metal is reflected as elliptically polarised with major axis rotated relative to the incident polarisation.

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