Nonlinear Magneto-Optical Response of $s$- and $d$-Wave Superconductors

J. Schmalian and W. Hübner

Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

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Abstract

The nonlinear magneto-optical response of $s$- and $d$-wave superconductors is discussed. We carry out the symmetry analysis of the nonlinear magneto-optical susceptibility in the superconducting state. Due to the surface sensitivity of the nonlinear optical response for systems with bulk inversion symmetry, we perform a group theoretical classification of the superconducting order parameter close to a surface. For the first time, the mixing of singlet and triplet pairing states induced by spin-orbit coupling is systematically taken into account. We show that the interference of singlet and triplet pairing states leads to an observable contribution of the nonlinear magneto-optical Kerr effect. This effect is not only sensitive to the anisotropy of the gap function but also to the symmetry itself. In view of the current discussion of the order parameter symmetry of High-$T_c$ superconductors, results for a tetragonal system with bulk singlet pairing for various pairing symmetries are discussed.

74.25.Gz, 74.25.-q, 74.25.Nf, 78.20.Ls

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I. INTRODUCTION

The investigation of the symmetry of the superconducting order parameters is currently one of the most exciting problems in the field of high-$T_c$ research.\textsuperscript{1–9} Many experiments suggest that the order parameter is anisotropic.\textsuperscript{1–5} Furthermore, the observation of $\pi$ phase shifts in corner junctions\textsuperscript{6,8,9} is consistent with a $d_{x^2-y^2}$ symmetry of the gap function, although another experiment\textsuperscript{7} favors a more conventional s-wave pairing. On the other hand, the occurrence of a finite tunneling current perpendicular to the planes\textsuperscript{10} seems to be incompatible with $d$-wave symmetry in a simple picture. In view of this debate, it is important to develop alternative experimental techniques which are able to discriminate between the various symmetries of the gap function. In particular, it is interesting to measure the symmetry of the gap function without the necessity of a tunneling contact, which always includes the problems of a residual magnetic field, trapped flux in the tunneling circuit, or singularities in the supercurrent flow at the corner\textsuperscript{11}.

On the other hand, optical second harmonic generation has widely been used as a probe for two dimensional optical, electronic and structural properties at various interfaces such as solid-vacuum, solid-gas, solid-solid, solid-liquid, or liquid-gas\textsuperscript{12,13}. Recently, the nonlinear magneto-optical Kerr-effect has become a new nonlinear optical method for the investigation of low-dimensional magnetic structures\textsuperscript{14–16}. This effect is interface sensitive within the electric dipole-approximation and directly probes, unlike methods based on Raman scattering, low-energy magnetic excitations ($\sim$ meV) using optical interband transitions ($\sim$ eV). In contrast to linear optical techniques, the nonlinear magneto-optical Kerr effect yields an excellent signal to noise ratio, since it is free of linear nonmagnetic background radiation. This advantage manifests itself both in the large magnetic intensity contrast upon magnetization inversion,

$$\frac{I(M) - I(-M)}{I(M) + I(-M)}$$

of about 40 % for Fe surfaces\textsuperscript{17,18} compared to a linear effect of typically 0.1 % and in a giant nonlinear Kerr rotation $\phi_{K}^{(2)}$ which, depending on the chosen Kerr-configuration, can
be tuned up to 90° nearly at will\textsuperscript{19−21}. This corresponds to an enhancement by 2 - 3 orders of magnitude compared to the usual linear Kerr rotation, which is even reduced in thin films. Thus, it allows for the determination of the magnetic interface symmetry, including the magnetic “easy axis”\textsuperscript{22}.

It is well-known that the symmetry of the nonlinear optical susceptibility is strongly affected by a magnetization or an external applied magnetic field.\textsuperscript{14} Thus it is of considerable interest to extend the symmetry analysis of the nonlinear magneto-optical response to the superconducting state for different symmetries of the superconducting order parameter. Therefore, we propose in this paper a new theory for the nonlinear optical response of a superconductor in the presence of a magnetic field, which is able to distinguish between certain symmetries of the gap function and might stimulate corresponding experiments. In the following, we present our theory and show that indeed a symmetry dependent contribution to the magneto-optical response without tunneling contact results in optical second harmonic generation. Although it is, due to the gauge invariance, impossible to measure the phase of the superconducting order parameter without tunneling contact, it is still possible to measure its symmetry, not solely its magnitude. This results from the interference of different pairing amplitudes in the dipole matrix elements of the three transitions in nonlinear optics. Due to the surface sensitivity of nonlinear optics for systems with bulk inversion symmetry, one can take advantage of the broken inversion symmetry at the surface. This is of interest, because Cooper pairing, together with the always present spin-orbit coupling, is then no more purely singlet- or triplet-like. The interference of the singlet and triplet pairing states, which is linear in spin-orbit interaction, leads to the symmetry sensitive contribution of the nonlinear optical response for systems in an external magnetic field. Note that the possible importance of mixed singlet and triplet pairing states at the interface of a tunneling contact between a heavy fermion and a conventional superconductor has already been discussed by Fenton\textsuperscript{23}. In order to obtain a more systematic insight into these phenomena, we perform the description of a superconductor at the surface of a bulk inversion symmetric system, including spin-orbit interaction and give a group-theoretical classification of the irreducible
representations of the gap function. This is of importance for a detailed calculation of the tensor elements of the nonlinear optical susceptibility which is performed in the second part of the theory. Finally, we present our results concerning the symmetry dependence of the corresponding experiment and discuss in detail the differences of the line shapes of the optical spectra. We find that it is possible to discriminate between an isotropic s-wave, a $s_{x^2+y^2}$- or $d_{x^2-y^2}$- wave and a $d_{xy}$- wave. However, no symmetry dependent differences between the $s_{x^2+y^2}$- and the $d_{x^2-y^2}$- waves occur, which are actually the most discussed symmetries of the high-T$_c$ systems. Nevertheless nonlinear magneto-optics is shown to be an alternative and complementary method to gain insight into the symmetry of the superconducting gap function.

II. THEORY

The strategy of this section is to calculate the effects of s- and d-wave superconductivity on the nonlinear optical susceptibility tensor $\chi^{(2)}$, which are due to (a) the modification of the bandstructure and thus the resonance denominators and (b) due to the symmetry of the superconducting order-parameter affecting the wave functions of the optical electric-dipole transition matrix elements. Thus, we proceed as follows: (i) First we set up the superconducting BCS-type Hamiltonian and perform its group theoretical analysis. In order to obtain the desired sensitivity of nonlinear optics to the symmetry of the gap function this requires, as it will turn out, the simultaneous absence of inversion symmetry, presence of an external magnetic field breaking time reversal, and spin-orbit interaction coupling singlet and triplet pairs. (ii) Making use of this symmetry classification and the mentioned constraints we then calculate the nonlinear magneto-optical response in s- and d- wave superconductors from the appropriate current-current-current correlation function and propose a suitable experimental geometry for the observation of this new nonlinear magneto-optical effect in superconductors.

In our theory for the nonlinear magneto-optical response of unconventional superconduct-
tors, the superconducting state is described within the BCS theory\textsuperscript{24}. The corresponding Hamiltonian with arbitrary pairing symmetry and in a magnetic field $\vec{h}$ is given by

$$H = \sum_{k\mu} \Psi_{k\mu}^\dagger \mathcal{H}_{k\mu} \Psi_{k\mu},$$  \hspace{1cm} (1)

with the four-component Nambu spinor $\Psi_{k\mu} = (c_{k\mu\uparrow}, c_{k\mu\downarrow}, c_{-k\mu\uparrow}^\dagger, c_{-k\mu\downarrow}^\dagger)$. Here, $c_{k\mu\sigma}^\dagger$ is the creation operator of an electron with momentum $k$, band index $\mu$ and spin $\sigma$. The $(4 \times 4)$ matrix $\mathcal{H}_{k\mu}$ can be expressed in terms of $(2 \times 2)$ block matrices:

$$\mathcal{H}_{k\mu} = \begin{pmatrix} \varepsilon_{k\mu} \hat{\sigma}^\sigma - \vec{h} \cdot \hat{\sigma} & \hat{\Delta}_{k\mu} \\ -\hat{\Delta}^*_{-k\mu} & -\varepsilon_{k\mu} \hat{\sigma}^\sigma + \vec{h} \cdot \hat{\sigma}^* \end{pmatrix}. \hspace{1cm} (2)$$

The block matrices are expanded in terms of the unit matrix $\hat{\sigma}^o$ and the vector of the Pauli matrices $\hat{\sigma}$. This notation is close to that of Sigrist and Ueda\textsuperscript{25}. The symmetry of the superconducting order parameter is characterized by the gap function $\Delta_{\sigma\sigma'}_{k\mu}$; $\langle c_{k\sigma\mu} c_{-k\sigma'\mu} \rangle$. We neglect any diamagnetic, i.e. Meissner effect of the magnetic field, but assume a large penetration depth at the surface and no influence of the vortex structure to the optical spectrum. This seems to be reasonable at least for the excitations in the interband regime discussed in this paper. $\Delta_{\sigma\sigma'}_{k\mu}$ is decomposed in the usual way in singlet states ($\Delta^o_{k\mu} = \Delta^o_{-k\mu}$) and triplet states ($d_{k\mu} = -d^*_{-k\mu}$):

$$\hat{\Delta}_{k\mu} = \left( \Delta^o_{k\mu} \hat{\sigma}^\sigma + d_{k\mu} \cdot \hat{\sigma} \right) i\hat{\sigma}^y. \hspace{1cm} (3)$$

The symmetry of $\Delta^o_{k\mu}$ and $d_{k\mu}$ with respect to the transition from $k$ to $-k$ is a direct consequence of the Pauli principle. Since we consider the states at a surface, $k$ refers to the two dimensional in-plane momentum.

Below the transition temperature $T_c$, the symmetry of a system is reduced compared to the high temperature phase. The symmetry group $G$ of the high temperature phase is determined by the symmetry operations which keep the Hamiltonian for $\hat{\Delta}_k = 0$ invariant. We consider a system which is for $\vec{h} = 0$ invariant with respect to the group

$$G = g \times K \times U(1), \hspace{1cm} (4)$$
where $g$, $K$ and $U(1)$ are the point group, time reversal operation and the gauge group of multiplication of electron creation operator by an arbitrary phase, respectively. In the ordinary case the normal-state gauge symmetry is broken at the superconducting phase transition, i.e. the residual symmetry group is $g \times K$. This is called a conventional superconductor. In unconventional superconductors however, the symmetry is lower than $g \times K$. At the transition temperature, the BCS gap equation is an eigenvalue equation and consequently, an eigenvector $\Delta_{\sigma' \sigma; \mathbf{k}_\mu}$ belongs to one of the irreducible representations $\mathcal{D}$ of the group $G$. If $\mathcal{D}$ is the unit representation $\mathcal{A}_1$ (or $\mathcal{A}_{1g}$ for systems with inversion symmetry) conventional superconductivity occurs. In all other cases the superconductivity is unconventional. In order to discuss the various symmetry states of the order parameter, one has to generate all irreducible representations of the gap function, where, due to spin-orbit coupling, the spin degrees of freedom cannot be transformed independently from the spatial (orbital) coordinates. For various point groups this symmetry classification has been performed. In all these cases the inversion operation $C_\text{i}$ is an element of the group $G$. Since we are interested in the investigation of superconducting properties with surface sensitive nonlinear optical experiments, we have to take the effect of broken inversion symmetry into account. In order to be specific, we consider the surface of a tetragonal system (bulk point group $D_{4h}$) with residual point group $C_{4v}$. This group has five irreducible representations: four of dimension one ($\mathcal{A}_1$, $\mathcal{A}_2$, $\mathcal{B}_1$ and $\mathcal{B}_2$) and one of dimension two ($\mathcal{E}$). The isotropic $s_o$ and and anisotropic $s_{x^2+y^2}$ s-waves transform as $\mathcal{A}_1$, the $d_{x^2-y^2}$-wave as $\mathcal{B}_1$, the $d_{xy}$-wave as $\mathcal{B}_2$, a $d_{x^2-y^2}d_{xy}$-wave as $\mathcal{A}_2$ and the $p_x$, $p_y$ waves as $\mathcal{E}$.

In order to classify the irreducible representations of the gap function, we have to analyze the transformation properties of $\Delta_{\sigma' \sigma; \mathbf{k}_\mu}$. Applying an element $R$ of the point group to $\hat{\Delta}_{\mathbf{k}_\mu}$, the following transformation of the singlet and triplet part results:

$$R \hat{\Delta}_{\mathbf{k}_\mu} = \left( \Delta^{\sigma}_{\mathcal{D}^{(1)}_R \mathbf{k}_\mu} + \tilde{D}^{(1)}_R \mathcal{D}^{(1)}_{\mathbf{k}_\mu} \cdot \hat{\sigma} \right) i\sigma^y. \tag{5}$$

Here, $\mathcal{D}^{(1)}_R$ is the representation of $R \in G$ which transforms the coordinates. If one considers the transformation of a Pauli spinor with respect to a combination $R = R_o C_i$ of the inversion
operation $C_i$ and a rotation $R_o$, only the rotational part has to be applied to the spinor, i.e. the representation of $R$ in spin space is $D_R^{(1/2)}$. Consequently, for the vector in spin space $\tilde{d}_k$, the representation $\tilde{D}_R^{(1)} \equiv D_{R_o}^{(1)}$, where the inversion operation is replaced by the identical transformation, has to be applied. Therefore, one finds in the bulk of a system with inversion symmetry: $C_i \hat{\Delta}_{k\mu} = \left(\Delta^o_{k\mu} - \tilde{d}_k \cdot \hat{\sigma}\right) i\hat{\sigma}^y$, since the vector $\tilde{d}$ is not affected directly by the inversion operation. The minus sign results from the inversion of $k$ to $-k$. Consequently, in the bulk, the singlet and triplet part belong to different irreducible representations and either singlet or triplet superconductivity occurs. In distinction to this, a coexistence of singlet and triplet pairing states is possible for systems without inversion symmetry, i.e. at the surface. Now, the in-plane inversion operation can be realized by a rotation (rotation by $\pi$ with $z$-axis as rotation axis). This rotation transforms the vector $\tilde{d}$ to $-\tilde{d}$ and the minus sign of the transformation $k \to -k$ is canceled. Consequently, the irreducible representations of the gap function at the surface contain both, singlet and triplet parts.

From these considerations one obtains the irreducible representations of the gap function from the simultaneous Clebsch-Gordon coupling of orbital and spin degrees of freedom. The results for the simultaneously occurring singlet and triplet part of the pairing amplitude are given in the table. Sigrist and Rice$^{30}$ calculated the irreducible representations of the tetragonal group $D_{4h}$. Since $D_{4h} = C_{4v} \times C_i$, it is straightforward to check the above results by reducing the subduced representations of $D_{4h}$. One finds: $A_1 = A_{1g} \oplus A_{2u}$, $A_2 = A_{2g} \oplus A_{1u}$, $B_1 = B_{1g} \oplus B_{2u}$, $B_2 = B_{2g} \oplus B_{1u}$ and $E = E_g \oplus E_u$ which leads to the results of the table. Here, $g$ and $u$ refer to the irreducible representations of $D_{4h}$ with even and odd parity. The irreducible representations of table I are the possible symmetry states of a superconductor on the surface of a tetragonal system and with spin orbit interaction. If one neglects the spin orbit coupling, the spin and orbital degrees of freedom transform separately and the singlet and triplet pairing states decouple again. Therefore, for a bulk singlet superconductor, the simultaneously occurring triplet part at the surface is of the order of the spin-orbit interaction, and vice versa. In heavy fermion systems the spin-orbit interaction is large, but even in transition metals one expects this quantity to be of the order
of 50 meV which, although being smaller, has nevertheless dramatic consequences such as the reorientation of the magnetic easy axis in thin ferromagnetic films upon the increase of the film thickness or the rise of the temperature. Finally, we expect the spin-orbit induced triplet part to be observable if one considers a surface sensitive experiment such as second harmonic generation.

Based on these group theoretical classifications, we calculate now the nonlinear magneto-optical susceptibility tensor of a superconductor and focus on the interference of the simultaneously occurring singlet and triplet part of the gap function. The optical response in second harmonic generation can be obtained from the nonlinear current-current-current correlation function:

\[
\chi_{\alpha\beta\gamma}(q, \omega) = \int_{-\infty}^{\infty} \frac{d\epsilon}{\pi} \int_{-\infty}^{\infty} \frac{d\epsilon'}{\pi} \int_{-\infty}^{\infty} \frac{d\epsilon''}{\pi} I_{\alpha\beta\gamma}(q, \epsilon, \epsilon', \epsilon'') \times \frac{f(\epsilon'') - f(\epsilon')}{\omega + i\delta - \epsilon'' + \epsilon} - \frac{f(\epsilon') - f(\epsilon)}{\omega + i\delta - \epsilon' + \epsilon} \times \frac{f(\epsilon'')}{2(\omega + i\delta) - \epsilon'' + \epsilon}
\]

(6)

where \( f(\epsilon) \) is the Fermi function and the spectral function \( I_{\alpha\beta\gamma}(q, \epsilon, \epsilon', \epsilon'') \) is given by

\[
I_{\alpha\beta\gamma}(q, \epsilon, \epsilon', \epsilon'') = \text{Tr} \left( J_{-2q_{\alpha}} \phi(\epsilon) J_{q_{\beta}} \phi(\epsilon') J_{q_{\gamma}} \phi(\epsilon'') \right).
\]

(7)

\( J_{q_{\alpha}} \) is the \( \alpha \)-th component of the current operator

\[
\vec{J}_q = \sum_{k\sigma\mu\nu} \vec{J}_{k\mu\nu} c_{k+q\sigma\mu}^\dagger c_{k-\frac{q}{2}\sigma\nu},
\]

(8)

and \( \phi(\epsilon) = -\frac{1}{\pi} \text{Im}(\epsilon + i\delta + H)^{-1} \) is the density of states matrix with Hamiltonian \( H \) of Eq. 2. The trace has to be performed with respect to all single particle states, i.e. the momentum (\( k \)), band (\( \mu, \nu \)), spin (\( \sigma \)) and Nambu degrees of freedom. In the following, we consider only interband transitions \( \mu \neq \nu \), and the limit of the dipole approximation \( q \to 0 \) can be performed without special care for plasmonic excitations.

The evaluation of the trace of Eq. 7 is straightforward with the knowledge of the unitary transformation \( U_{k\mu} \), which diagonalizes \( H \) and \( \phi(\epsilon) \). In the following we discuss \( U_{k\mu} \) for a bulk singlet superconductor in the limit of weak spin-orbit interaction \( \lambda_{\text{s.o.}} \) and weak external
field because the phase sensitive contributions of the optical response vanish if either \( \lambda_{s.o.} \) or the magnetic field is zero. For weak external magnetic field, the eigenvalues are given by

\[
E_{k\mu} = \pm h \pm \varepsilon_{k\mu},
\]

where

\[
\varepsilon_{k\mu} = \sqrt{\varepsilon_{k\mu}^2 + \frac{1}{2} \text{tr} \left( \hat{\Delta}_{k\mu} \hat{\Delta}_{k\mu}^\dagger \right)}.
\]

\( h \) is the absolute magnitude of \( \vec{h} \) and \( \text{tr} \) denotes the trace in spin space. \( \hat{\Delta}_{k\mu} \) belongs to one of the irreducible representations of table I. Analogously, the unitary transformation is given by

\[
U_{k\mu} = U^\Delta_{k\mu} U^h_{k\mu},
\]

where \( U^\Delta_{k\mu} \) and \( U^h_{k\mu} \) are the transformations which diagonalize \( \mathcal{H}_{k\mu} \) for \( \vec{h} = 0 \) and \( \vec{d}_{k\mu} = 0 \), respectively. This is correct up to first order in \( \lambda_{s.o.} \) and \( \vec{h} \). The zero-field transformation \( U^\Delta_{k\mu} \) can be expressed in terms of \((2 \times 2)\) matrices \( \hat{u}_{k\mu} \) and \( \hat{v}_{k\mu} \):

\[
U^\Delta_{k\mu} = \begin{pmatrix}
\hat{u}_{k\mu} & \hat{v}_{k\mu} \\
\hat{v}^*_{-k\mu} & \hat{u}^*_{-k\mu}
\end{pmatrix},
\]

where

\[
\hat{u}_{k\mu} = (\varepsilon_{k\mu} - \varepsilon_{k\mu}) / \varepsilon_{k\mu} \hat{\sigma}^a
\]

and

\[
\hat{v}_{k\mu} = -\hat{\Delta}_{k\mu} / \varepsilon_{k\mu}.
\]

Similar to the gap function in Eq. 3, these \((2 \times 2)\) matrices are expanded in Pauli matrices, leading to a singlet part \( v^a_{k\mu} \) and triplet part \( \vec{v}_{k\mu} \) of \( \hat{v}_{k\mu} \). The transformation \( U^h_{k\mu} \) is determined by a rotation in spin space

\[
U^h_{k\mu} = \begin{pmatrix}
\exp \left( -i\vec{a} \cdot \vec{\sigma} \right) & 0 \\
0 & \exp \left( i\vec{a} \cdot \vec{\sigma}^* \right)
\end{pmatrix},
\]
with rotation axis \( \vec{e}_a = -(\vec{e}_z \times \vec{e}_h)/|\vec{e}_z \times \vec{e}_h| \) and angle \( \cos(2a) = \vec{e}_z \cdot \vec{e}_h \) \((\vec{a} = a\vec{e}_a)\). \( \vec{e}_h \) is the unit vector in the direction of \( \vec{h} \). Using this transformation, we can diagonalize the Hamiltonian leading to the quasiparticle spinor

\[
\Psi_{k\mu} = U_{k\mu} \Phi_{k\mu} .
\]

(16)

Here the components of \( \Phi_{k\mu} \) are the destruction operators of the eigenstates with eigenvalues given in Eq. (9).

In order to express the current operator in terms of the Nambu spinors, we have to consider the behavior of the matrix element \( \tilde{J}_{k\mu\nu} \) under the simultaneous transformation \( k \rightarrow -k \) and \((\mu, \nu) \rightarrow (\nu, \mu)\):

\[
\tilde{J}_{-k\mu\nu} = p_{-k}^{\mu\nu} \tilde{J}_{k\nu\mu} .
\]

(17)

Although the phase factors \( p_{-k}^{\mu\nu} \) depend on the choice of the phase of the Wannier functions, all observable quantities like \( \chi_{\alpha\beta\gamma}(q, \omega) \) are independent of this choice. Now, the current operator can be expressed in terms of the Nambu spinors:

\[
\tilde{J} = \frac{1}{2} \sum_{k\mu\nu} \tilde{J}_{k\mu\nu} \Psi_{k\mu}^\dagger \left( \begin{array}{cc} \hat{\sigma}^o & 0 \\ 0 & -p_{-k}^{\mu\nu} \hat{\sigma}^o \end{array} \right) \Psi_{k\nu} ,
\]

(18)

and we find for the nonlinear spectral function of Eq. (7):

\[
I_{\alpha\beta\gamma}(\epsilon', \epsilon'') = \frac{1}{8} \sum_{k\mu\nu\kappa} \tilde{J}_{k\mu\nu} \tilde{J}_{k\nu\kappa} \tilde{J}_{k\kappa\mu} \times \text{Tr}' \left\{ \mathcal{M}_{k}^{\mu\nu} \varrho_{\kappa}(\epsilon) \mathcal{M}_{k}^{\nu\kappa} \varrho_{\kappa}(\epsilon') \mathcal{M}_{k}^{\kappa\mu} \varrho_{\kappa}(\epsilon'') \right\} .
\]

(19)

Here, \( \mathcal{M}_{k}^{\mu\nu} \) and \( \varrho_{\kappa}(\epsilon) \) are \((4 \times 4)\) matrices in Nambu and spin space, whereby

\[
\mathcal{M}_{k}^{\mu\nu} = U_{k\mu}^\dagger \left( \begin{array}{cc} \hat{\sigma}^o & 0 \\ 0 & -p_{-k}^{\mu\nu} \hat{\sigma}^o \end{array} \right) U_{k\nu} ,
\]

(20)

results from the transformation of Eq. (18) into the quasiparticle representation, where \( \varrho_{\kappa}(\epsilon) \) is diagonal. Consequently, the trace \( \text{Tr}' \) has to be performed with respect to the Nambu and spin degrees of freedom.
Nonlinear optics and in particular nonlinear magneto-optics offers a unique method to probe low-lying excitations close to the Fermi-level with optical photons, since SHG, which involves three photons, takes advantage of an additional degree of freedom that is absent in linear optics. Thus it allows to use conventional monochromatic, intense, and tunable pulse laser sources in the ps to fs regime such as mode-locked Ti-sapphire lasers. Besides, in nonlinear interband optics, there is no collective plasmon background which is material insensitive and may severely hamper the interpretation of linear optical experiments.

Therefore, we restrict ourselves to a special interband excitation process. We consider the transition from the initial state $i$ with energy $E_i \approx -3$eV, below the Fermi energy to the intermediate state $s$ at the Fermi level (which is the only superconducting state) and to the final state $f$ with energy $E_f \approx 3$eV above $E_F$, i.e. we consider $\mu = f$, $\kappa = s$, and $\nu = i$. A possible, but not necessary, origin of the states $i$ and $f$ might be due to the Mott-Hubbard splitting of the hybridized Cu 3$d_{x^2-y^2}$ and O 2$p_x(y)$ orbitals. Since the intermediate state is the only state with superconducting coherence, we skip the band index of the matrices $\hat{u}_k$ and $\hat{v}_k$. Performing finally the traces in Eq.(19), we obtain:

$$\chi_{\alpha\beta\gamma}(\omega) = \chi^{(0)}_{\alpha\beta\gamma}(\omega) + \chi^{(h)}_{\alpha\beta\gamma}(\omega) + \mathcal{O}(h^2) ,$$

where

$$\chi^{(0)}_{\alpha\beta\gamma}(\omega) = \sum_k j^{\alpha}_{kfi} j^{\beta}_{kis} j^{\gamma}_{ksf} \left( |u^\alpha_k|^2 G_1(k,\omega) + |v^\alpha_k|^2 G_2(k,\omega) \right)$$

is the zero field susceptibility tensor in second harmonic generation within the superconducting state which gives already a contribution without spin-orbit interaction. The nonvanishing tensor elements for $\chi^{(0)}_{\alpha\beta\gamma}(\omega)$ are the same as in the normal state ($\alpha\beta\gamma \in \{zzz, zxx, zyy, xzx, xxz, yzy, yyz\}$). This results here from the transformational properties of the three matrix elements $j^{\alpha}_{kfi} j^{\beta}_{kis} j^{\gamma}_{ksf}$, which transform as the corresponding combination of the coordinates $x_{\alpha} x_{\beta} x_{\gamma}$, even if a single matrix element e.g. $j^{\alpha}_{kfi}$ does not transform like $x_{\alpha}$. The functions $G_{1(2)}(k,\omega)$ result from the numerous combinations of Fermi functions and energy denominators which occur by performing the traces in spin and Nambu space.
\( \chi^{(h)}_{\alpha\beta\gamma}(\omega) \) is the new contribution of the magneto-optical Kerr effect in the superconducting state. This can be seen from the symmetry relations of the magneto-optical susceptibility

\[
\chi^{(h)}_{\alpha\beta\gamma}(\omega) = \sum_k j^{\alpha}_{ki} j^{\beta}_{k\alpha} j^{\gamma}_{k\beta} (v^0_k)^* \vec{v}_k \cdot \vec{e}_h F(k, \omega),
\]

which depends on the superconducting gap function not only through its magnitude but also through \( \Delta_k^\omega \) itself. Due to the additional triplet part however, the result is still gauge invariant. The function \( F(k, \omega) \) correspond to the \( G_{1(2)}(k, \omega) \) for \( \chi^{(h)}_{\alpha\beta\gamma}(\omega) \). Considering a magnetic field parallel to the x-axis (in plane), the nonvanishing elements of \( \chi^{(h)}_{\alpha\beta\gamma}(\omega) \) are: \( \alpha\beta\gamma \in \{yyy, xxy, xyx, yxx, zzy, zyz, yzz\} \). This results from the combination of the transformation properties of the normal state matrix elements and of the symmetry sensitive term \((v^0_k)^* \vec{v}_k \cdot \vec{e}_h \). Using Eq. (14), the \( k \)-dependence of the latter results from the irreducible representations given in table I.

The above matrix elements lead to a rotation of the polarization of the incident light due to the interference of the singlet and triplet states at the surface of a superconductor. Thus nonlinear magneto-optics, unlike linear optical probes, provides indeed an optical method to discriminate different superconducting pairing symmetries by exclusively employing the effect of optical photons to low energy excitations. In the next paragraph, we discuss the numerical results of the above model bandstructure for the most realistic experimental setups and show how experiments can distinguish between certain symmetries of the gap function using nonlinear magneto-optics.

### III. RESULTS

In this section we discuss the numerical results obtained for the tensor elements \( \chi^{(0)}_{zzz} \) of second harmonic generation without magnetic field and \( \chi^{(h)}_{yzz} \) which gives rise to the rotation of the polarization plane for an applied magnetic field parallel to the x-axis. For simplicity we neglect the dispersion of the initial and the final state and consider solely the \( k \)-dependence which results from the superconducting gap function. The momentum summations are performed within the two dimensional Brillouin zone using \( 81 \times 81 \) \( k \)-points.
The calculations are performed for a magnetic field of 9 T (corresponding to a field induced band splitting of 0.5 meV) and a temperature of 1.5 K. The magnitude of the singlet part of the gap function is assumed to be 5 meV. Furthermore, the magnitude of the dipole matrix elements is estimated to be $10^{-11}$ m. All results presented here are not sensitive to the specific set of parameters chosen, but are typical for reasonable values of the corresponding energy scales. This was checked by systematically varying the dependence of the nonlinear susceptibility on the magnitude of the gap function, the magnetic field, the position of the initial and final states $E_i$ and $E_f$, the temperature and the linewidth broadening $\delta$.

In Figs. 1(a) and (b), we show $\omega^2 \text{Im} \chi^{(o)}_{zzz}(\omega)$ and $\omega^2 \text{Im} \chi^{(h)}_{yyz}(\omega)$ for an isotropic $s$-wave. For the conventional SHG, we find a line shape similar to the real part of a Lorentzian, which is typical for a three level system discussed in this paper. More interestingly, the fine structure of the peak, shown in the inset of Fig. 1(a) clearly shows the energy scale of the superconducting gap. Comparing this behavior with the Kerr signal $\omega^2 \text{Im} \chi^{(h)}_{yyz}(\omega)$ of Fig. 1(b), one finds that the interference of the singlet and triplet pairing states leads to a line shape with several pronounced zeros and with a fine structure that yields, besides the energy scale of the superconducting gap, also excitations which result from the magnetic field splitting. In all our calculations, this line shape was exclusively observed for an isotropic $s$-wave and can be considered as a fingerprint of this symmetry.

In Figs. 2 and 3, the corresponding results for the anisotropic $s$-wave and the $d_{x^2-y^2}$-wave are shown. Although the result for the conventional SHG is similar to that of the isotropic $s$-wave, a totally different line shape of the Kerr signal results. This is due to the symmetry dependent prefactor in $\chi^{(h)}_{yz} (\omega)$ and can be used to discriminate these two symmetries from the isotropic $s$-wave. Furthermore the fine-structure of these two symmetries is very different from the isotropic $s$-wave. Due to the occurrence of nodes in the gap, not only a peak but a whole broad band between 3 eV and 3.01 eV is observable. This range is surprisingly given by twice the superconducting gap magnitude. Unfortunately, there are only slight differences between the two symmetries shown in Fig. 2 and 3. This is due to the similar $\mathbf{k}$-dependence
of the triplet part given in table I. Only the fine structure of the peaks displayed in the insets of Fig. 2(b) and 3(b) exhibits a clear difference, where the anisotropic s-wave has a clear zero at 3.01 eV which is more or less smeared out for the \( d_{x^2-y^2} \) wave.

In this context it is of importance to compare these results to the usual nonlinear Kerr effect in the normal state in an external applied field which can be easily estimated using previous results by Pustogowa et al.\(^{31} \) as

\[
\frac{\chi^{(h)}_{yzz,\text{normal}}}{\chi^{(0)}_{yzz}} \approx \frac{\lambda_{s.o} J(h)}{(\hbar \omega)^2}.
\]

Here, the incident photon energy \( \hbar \omega \) at resonance is 3 eV, while the energy splitting \( J(h) \) caused by the external magnetic field \( h \) is 0.5 meV (see above). For this small value of \( J(h) \), the formula given in appendix C of the paper by Pustogowa et al. yields a linear dependence. Thus, we find \( \frac{\chi^{(h)}_{yzz,\text{normal}}}{\chi^{(0)}_{yzz}} \approx 2.7 \cdot 10^{-6} \) due to the absence of a spontaneous magnetization. From this estimate, it follows that the observability of the new contribution to the nonlinear Kerr effect is clearly guaranteed for the anisotropic s-wave. Although, the intensities of the other symmetries are smaller than the estimated value of the usual nonlinear Kerr effect in both the normal and superconducting state, we believe that this effect is still observable for the following reason: Due to the neglect of the dispersion of the states in our model bandstructure, the disappearance of the signal results from cancellations of contributions of the order of magnitude of the anisotropic s-wave in the \( \mathbf{k} \)-summation. This is due to the artificially high symmetry of this bandstructure. The simplified description of the high-\( T_c \) materials is used because the aim of this paper is to demonstrate the strong interdependence of the lineshape of the nonlinear magneto-optical susceptibility and the symmetry of the superconducting state. A more realistic bandstructure immediately leads to larger intensities of \( \chi^{(h)}_{yzz} \), while keeping the characteristics of the line shapes of the spectra.

In Fig. 4 we finally show our results for the \( d_{xy} \) symmetry. Although, this symmetry does not seem to be the most probable candidate for the high-\( T_c \) materials, it shows most clearly the symmetry dependence of the nonlinear magneto-optical Kerr effect. In contrast to the anisotropic s-wave and the \( d_{x^2-y^2} \) wave, there occurs a sign change between the
magnetic and nonmagnetic optical spectrum. This is observable since the sign of the Kerr spectrum determines the direction of the rotation of the polarization axis, i.e. the Kerr angle. Furthermore, the satellites shown in the inset of Fig. 4(a) and (b) cover only the range from 3 eV to 3.005 eV, i.e. only one times the gap magnitude.

For the existence of a finite Kerr signal, it is necessary to break time reversal symmetry and to apply an external magnetic field. This enables one to keep any direction of the field fixed and to study the anisotropy of the effects discussed in this paper. However, due to the strong but short-ranged antiferromagnetic correlations it might also be possible to take advantage of the locally broken time-reversal symmetry of the high-\( T_c \) materials. Since a finite Kerr signal is expected for certain long-range ordered antiferromagnets\(^{32} \), a pump-and-probe experiment (on a time scale faster than the average lifetime of the local spin configurations \( \tau_{\text{spin}} \approx 10^{-12} - 10^{-13} \) s) could be able to resolve the influence of the neighboring spins on the site which is excited by the optical excitation. Furthermore, for a practical realization of the experiment, one has to take into account the possible heating effects of the incoming light on the sample, which might lead to a local disappearance of the superconducting state. In view of the comparable excitation energies of the nonlinear magneto-optical Kerr effect in ferromagnets, we believe that this effect is of minor importance, since for fs laser pulses sample heating is of the order of 10 K and thus negligible. This simple estimate is readily obtained from the comparison of laser heating with ns pulses\(^{33} \) yielding intensities of 100 MWm\(^{-2} \) and temperature rises of the order of 100 K and typical fs measurements of the nonlinear Kerr-effect\(^{21} \) which operate at laser powers as low as 100 mW focused on spot diameters of 100 \( \mu \)m.

In conclusion, we presented a theory for the nonlinear magneto-optical response of superconductors. The surface sensitivity of this experiment is of particular interest for the simultaneous occurrence of singlet and triplet pairing amplitudes. Therefore, a suitable material for this experiment is the Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_8\) compound, where almost no reconstruction of the cleaved surface (Bi-O layer) occurs, and where the existence of the superconducting state in the upper CuO\(_2\) layer was clearly shown in photoemission experiments.\(^2 \). Since, due
to difficulties in the manufacture of the tunneling contacts, all corner junction experiments where so far performed with YBa$_2$Cu$_3$O$_{7-\delta}$ samples, this gives also insight into the symmetry of another class of cuprate compounds. Note that furthermore the surface sensitivity does not depend on the actual depth beneath the surface where superconductivity starts, since the electronic symmetry of the superconducting state surface is of relevance in this context which may or may not be perfectly identical to the physical surface. On the other hand the new nonlinear magneto-optical effect proposed in this paper may also be of considerable importance for interfaces between $s$- and $d$-wave superconductors. Furthermore, we performed a group-theoretical classification of the irreducible representations of the gap function at the surface of a tetragonal system. Based on this theory, we showed that the interference of singlet and triplet pairing states in a magnetic field leads to a new contribution to the nonlinear magneto-optical Kerr signal which is sensitive to certain symmetries of the superconducting order parameter rather than only to its magnitude. This enables us to give the basic line shapes of the corresponding optical spectra and to show that it is possible to discriminate an isotropic $s$-wave and a $d_{xy}$ wave from the anisotropic $s_{x^2+y^2}$ and $d_{x^2-y^2}$ waves. Unfortunately, it is not possible to discriminate between the two latter symmetries which seem to be the most probable symmetries of the high-\(T_c\) materials. Nevertheless, we believe that the nonlinear optic can yield information complementary to the tunneling experiments and might be also of importance in view of the application on heavy fermion superconductors, where it was also manifested that the superconducting state is anomalous$^{34-36}$.

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REFERENCES

1 J. A. Martindale, S. E. Barrett, C. A. Klug, K. E. O’Hara, S. M. DeSoto, C. P. Slichter, T. A. Friedmann, and D. M. Ginsberg, Phys. Rev. Lett. 68, 702 (1992).

2 Z.-X. Shen, D. S. Dessau, B. O. Wells, D. M. King, W. E. Spicer, A. J. Arko, D. Marshall, L. W. Lombardo, A. Kapitulnik, P. Dickinson, S. Doinach, J. DiCarlo, T. Loeser, and C. H. Park, Phys. Rev. Lett. 70, 1553 (1993).

3 W. N. Hardy, D. A. Bonn, D. C. Morgan, R. Liang, and K. Zhang, Phys. Rev. Lett. 70, 3999 (1993).

4 J. Kane, Q. Chen, K.-W. Ng, and H.-J. Tao, Phys. Rev. Lett. 72, 128 (1994).

5 T. P. Devereaux, D. Einzel, B. Stadlober, R. Hackl, D. H. Leach, and J. J. Neumeier, Phys. Rev. Lett. 72, 396 (1994).

6 D. A. Wollman, D. J. Van Halingen, W. C. Lee, D. M. Ginsberg, and A. J. Leggett, Phys. Rev. Lett. 71, 2134 (1993).

7 P. Chaudhari and Shawn-Yu Lin, Phys. Rev. Lett. 72, 2134 (1994).

8 D. A. Brawner and H. R. Ott, Phys. Rev. B 50, 6530 (1994).

9 C. C. Tsuei, J. R. Kirtley, C. C. Chi, Lock See Yu-Jahnes, A. Gupta, T. Shaw, J. Z. Sun, and M. B. Ketchen, Phys. Rev. Lett. 73, 593 (1994).

10 D. A. Gajewski, M. B. Maple, and R. C. Dynes, Phys. Rev. Lett. 72, 2267 (1994).

11 For a detailed and recent discussion see: D. J. Van Harlingen, Rev. Mod. Phys. 67, 523 (1995).

12 Y. R. Shen, Ann. Rev. Mater. Sci. 16, 69 (1986).

13 G. L. Richmond, J. M. Robinson, and V. L. Shannon, Prog. Surf. Sci. 28, 1 (1988).

14 R.-P. Pan, H. D. Wei, and Y. R. Shen, Phys. Rev. B39, 1229 (1989).
15 W. Hübner and K.-H. Bennemann, Phys. Rev. B 40, 5973 (1989).

16 W. Hübner, Phys. Rev. B 42, 11553 (1990).

17 J. Reif, J. C. Zink, C.-M. Schneider, and J. Kirchner, Phys. Rev. Lett. 67, 2878 (1991).

18 W. Hübner and K.-H. Bennemann, Vacuum 41, 514 (1990).

19 U. Pustogowa, W. Hübner, and K.-H. Bennemann, Phys. Rev. B 49, 10031 (1994).

20 H. A. Wierenga, W. de Jong, M. W. J. Prins, Th. Rasing, R. Vollmer, A. Kirilyuk, H. Schwabe, and J. Kirchner, Phys. Rev. Lett. 74, 1462 (1995).

21 B. Koopmans, M. Groot Koerkamp, Th. Rasing, and H. van den Berg, Phys. Rev. Lett. 74, 3692 (1995).

22 W. Hübner and K.-H. Bennemann, to be published in Phys. Rev. B (1995).

23 E. W. Fenton, Solid State Commun. 54, 709 (1985); Physica B 135, 60 (1985).

24 J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

25 M. Sigrist and K. Ueda, Rev. of Modern Physics 63, 239 (1991).

26 P. W. Anderson, Phys. Rev. B 32, 2935 (1985).

27 G. E. Volovik and L. P. Gorkov, Sov. Phys. JETP 61, 843 (1985).

28 E. I. Blount, Phys. Rev. B 32, 2935 (1985).

29 M. Sigrist and T. M. Rice, Phys. Rev. B 39, 2200 (1985).

30 M. Sigrist and T. M. Rice, Z. Phys. B 68, 9 (1987).

31 U. Pustogowa, W. Hübner, and K.-H. Bennemann, Phys. Rev. B 48, 8607 (1993).

32 M. Fiebig, D. Fröhlich, B. B. Krichevtsov, and R. V. Pisarev, Phys. Rev. Lett. 73, 2127 (1994).
33 A. Vaterlaus, T. Beutler, and F. Meier, Phys. Rev. Lett. 679, 3314 (1991).

34 D. J. Bishop, C. M. Varma, B. Batlogg, E. Bucher, Z. Fisk, J. L. Smith, Phys. Rev. Lett. 53, 1009 (1984).

35 C. L. Broholm, G. Aeppli, R. N. Kleiman, D. R. Harshman, D. J Bishop, E. Bucher, D. Ll. Williams, E. J. Ansaldo, R. H. Heffner, Phys. Rev. Lett. 65, 2062 (1990).

36 R. N. Kleiman, C. Broholm, G. Aeppli, E. Bucher, N. Stucheli, D. J. Bishop, K. N. Clausen, K. Mortensen, J. S. Pedersen, B. Howard, Phys. Rev. Lett. 69, 3120 (1992).
| irred. representation | singlet part                                                                 | triplet part                                     |
|-----------------------|------------------------------------------------------------------------------|-------------------------------------------------|
| $\mathcal{A}_1$       | $const. \cdot \cos(k_x) + \cos(k_y)$                                        | $\vec{e}_x \sin(k_y) - \vec{e}_y \sin(k_x)$    |
| $\mathcal{A}_2$       | $(\cos(k_x) - \cos(k_y)) \sin(k_x) \sin(k_y)$                              | $\vec{e}_x \sin(k_x) + \vec{e}_y \sin(k_y)$    |
| $\mathcal{B}_1$       | $\cos(k_x) - \cos(k_y)$                                                     | $\vec{e}_x \sin(k_y) + \vec{e}_y \sin(k_x)$    |
| $\mathcal{B}_2$       | $\sin(k_x) \sin(k_y)$                                                      | $\vec{e}_x \sin(k_x) - \vec{e}_y \sin(k_y)$    |
| $\mathcal{E}$         | $\sin(k_x) \sin(k_z), \sin(k_y) \sin(k_z)$                                | $\vec{e}_z \sin(k_x), \vec{e}_z \sin(k_y)$     |

TABLE I. Singlet and triplet parts of the gap function for the irreducible representations of the point group $C_4$. $k_x$ and $k_y$ are the components of the in plane momentum. $k_z$ represents an additional quantum number, which changes sign if one interchanges the two paired electrons and which is related to the layer index at the surface.
FIGURES

FIG. 1. \(\omega^2\text{Im}\chi_{zzz}(\omega)\) (a) and \(\omega^2\text{Im}\chi_{yzz}(\omega)\) (b) for an isotropic s-wave symmetry of the gap function. Note the very different line shapes of the two experiments, typical for the isotropic s-wave. The insets show the fine structure of the results near the excitation energy of 3 eV. For better visibility the spectra are artificially broadened by a Lorentzian width \(\delta\) of 50 meV in the main figures and of 0.5 meV in the insets throughout. Consequently, the inset peak heights differ from those of the main figures.

FIG. 2. As in Fig. 1, but for an anisotropic \(s_{x^2+y^2}\) wave. Note the difference of the magnetic line shape compared to the isotropic s-wave and the broad fine structure up to two times the magnitude of the gap, shown in the inset.

FIG. 3. As in Fig. 1, but for a \(d_{x^2-y^2}\) wave. The spectra are very similar to the \(s_{x^2+y^2}\) wave, which results from the similar \(k\)-dependence of the triplet pairing amplitude, given in the table. Slight differences occur for the fine structure near 3 eV.

FIG. 4. As in Fig. 1, but for a \(d_{xy}\) wave. In distinction to the \(s_{x^2+y^2}\) and \(d_{x^2-y^2}\) wave, the signs of the nonmagnetic and magnetic spectra are different. Furthermore the satellites shown in the inset occur only up to the magnitude of the gap function.
Energy $E$ (eV) vs. $\omega^2 \text{Im} \chi^{(2)}_{\text{SHG}}(\omega)$ (s$^2$/m$^2$).

isotropic s-wave

$\omega^2 \text{Im} \chi^{(2)}_{\text{SHG}}(\omega)$ (s$^2$/m$^2$):

- $8 \times 10^{19}$
- $4 \times 10^{19}$
- $2 \times 10^{19}$
- $0$
- $-2 \times 10^{19}$
- $-4 \times 10^{19}$
- $-6 \times 10^{24}$

Energy $E$ (eV):

- $3.004$
- $3.005$
- $3.006$
isotropic s-wave
anisotropic s-wave
\( \omega^2 \text{Im} \chi_{\text{SHG}}^{(2)}(\omega) \) (s\(^2\)m)
$\omega^2 \text{Im} \chi_{\text{mag}}^{(2)}(\omega)$ (s$^2$/m$^2$)

$d_{x^2-y^2}$ - wave

Energy E (eV)
\[ \omega^2 \text{Im} \chi_{\text{mag}}^{(2)}(\omega) \left( \text{s}^{-2} \text{m} \right) \]

Energy \( E \) (eV)

\[ d_{xy} - \text{wave} \]