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On the use of twisted photons for spectroscopy of impurity centers in crystals

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Absorption of twisted photons for quadrupole ${}^4f$ - ${}^4f$ transitions in Re^{3+} impurity ions in micro- and macrocrystals is considered. Two types of twisted photon beams—the Laguerre-Gaussian and the Bessel-Gaussian beams—are considered and compared. Twisted photons have a nonzero transverse field gradient, which leads to selection rules for quadrupole transitions other than those in the case of the usual quadrupole transitions caused by a longitudinal field gradient. This allows one to observe new spectral lines which are absent in the usual absorption spectra. For microcrystals placed at the beam axis of twisted photons the otherwise dominating forced dipole ${}^4f$ - ${}^4f$ transitions are absent, which simplifies the observation of new spectral lines.

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I. INTRODUCTION

In recent years, there has been considerable interest in the optical fields that carry an optical orbital angular momentum and have helical phase fronts (see, e.g., [1–15] and references therein). The orbital angular momentum (OAM), together with spin angular momentum from light circular polarization, contributes to the overall angular momentum of a light beam and becomes thus important in various light-matter interaction processes. In particular, the OAM can be transferred to the external angular momentum of a free atom if the size of the wave function of its external motion is comparable or larger than λ [2]. This may take place, e.g., in the case of atomic Bose-Einstein condensate [12].

On the quantum level, the light beam with OAM l may be considered as a ray of photons having the momentum $l\hbar$ in addition to the spin momentum (polarization) $\hbar$ per photon [1–5]. Such photons are called "twisted" photons [3]. The twisting of photons shows up at a distance of $\sim \lambda/|l|$. This $\gtrsim\lambda$ scale of twisting raises the question of whether the twisting is able to affect the optical transitions in atoms. In other words, is an atom too small to "feel" this lengthy twist of photons, or not? Here we have in mind atoms localized in space (e.g., in solids).

Recently it was shown that the dipole-allowed optical transitions in atoms in solids are not affected by the OAM (twist) (see, e.g., [6]). However, the dipole-forbidden but quadrupole-allowed transitions in localized atoms can "feel" the OAM if the beam waist w_0 is sufficiently small [7–11]. It becomes possible because the quadrupole transitions take place due to the gradient of the electromagnetic field, and the OAM affects this gradient. Moreover, the OAM is ultimately associated with the field gradient. This gradient differs from the field gradient of usual plane waves: The OAM gradient is directed perpendicularly to the propagation direction, while for nontwisted light the essential gradient is directed along the beam propagation. This difference results in different selection rules for optical transitions, and makes it possible to distinguish twisted and nontwisted photons. For example, for free atoms in the external magnetic field the use of twisted photons propagating along this field allowed the observation of optical transitions forbidden in the case of nontwisted photons [6,11,13–15]. The spectral lines corresponding to these transitions can be distinguished from other allowed transitions due to the Zeeman splitting as was done in Ref. [15], where an additional quadrupole transition at 729 nm was observed in Ca^+ spectra under excitations by twisted photons.

In this report, we are considering the absorption of twisted photons by impurity centers in crystals due to quadrupole-allowed transitions in these centers. We show that the spectra for twisted photons depend on the absolute value $|l|$ of twisted photons. The dependence on the sign of l is absent, which is a consequence of the small size of the centers, as compared to the spatial size of the twist. An exception arises for the centers located exactly at the axis of the beam of twisted photons; these centers can also "feel" the sign of the OAM l. However, the number of such centers is negligibly small.

In a nano- or microcrystal placed close to the symmetry axis of the beam with OAM $|l| = 1$ the field takes the zero value, but the transverse gradient achieves the maximum value (for beams possessing $|l| > 1$ this component of the field gradient is zero at the axis). In this case, the intensities of new lines in the spectra of quadrupole-allowed transitions are maximal. Outside the axis, the transverse field gradient exists for any l. Therefore, for macroscopic crystals the absorption in new spectral transitions exists for any l.

Two types of light beams with OAM will be considered: the Laguerre-Gaussian (LGBs), and the Bessel-Gaussian (BGBs) beams. To calculate the field gradient for LGBs, we take into account that the mathematical expression for the Laguerre-Gaussian beam, after a proper transformation of variables, reduces (up to a normalization factor) to the eigenfunctions of a dimensionless twofold degenerate harmonic oscillator. These functions are orthogonal and normalized, which essentially simplifies the calculations of the field gradient for LGBs and the corresponding matrix elements of absorption. BGBs with OAM are more tightly focused than LGBs with the same Gaussian envelope; therefore, for $|l| = 1$ and $p > 0$ they have also a larger field gradient in the beam center than LGBs. In addition, BGBs with inclination angles close to $\pi/2$ have a strongly reduced longitudinal gradient. As a result, within the axial region of such beams only new quadrupole transitions, initiated by the transverse field gradient, take place while the dipole transitions and the usual quadrupole transitions due to the longitudinal field gradient are absent. New spectral transitions can be observed also for beams without OAM but with a transverse field gradient. The brief discussion of the use of the Hermite-Gaussian beams without OAM is given in the Appendix.

As a promising object for observation of the effects of OAM in absorption spectra, we consider the impurity centers of triply charged ions of rare-earth (RE) atoms in crystals that have ^4f-^4f optical transitions. An example is the cubic symmetry optical center in the Nd^{3+}-doped CaF$_2$. These centers have a very long (tens of milliseconds) spontaneous emission lifetime and low spontaneous emission dipole transition rates, because they are parity forbidden [16]. In some cases, using ordinary light for excitation, one cannot see all possible optical transitions between the crystal-field splitting states of various RE manifolds in dielectric crystals, the number of which is determined by the maximum possible splitting in the crystal field [which is $2J+1$ for non-Kramers ions and $(2J+1)/2$ for the Kramers ions]. In these cases, photons with OAM can allow quadrupole transitions between these states: Twisted photons can result in new transitions corresponding to different values of the projections m of the total momentum J of ^4f electrons on the symmetry axis in the initial and final states. These transitions result in the appearance of new narrow lines in optical spectra and make hitherto invisible crystal-field splitting states visible.

We should also note the Re^{3+} ions in LiYF$_4$ and other crystals with a similar structure. At least some of these centers have an inversion symmetry (point group S_4) and strongly forbidden dipole transitions. In these centers, the selection rules for the magnetic quantum number m also depend on the direction of the light field gradient. Therefore, the use of twisted photons with their specific field gradient can initiate transitions forbidden for ordinary nontwisted photons.

In this connection, especially interesting would be the experiments with nano- or microcrystals placed at the beam axis. In this case, the forced dipole transitions, giving (according to the Judd and Ofelt theory [17–19]) an essential contribution to the spectra of the ^4f-^4f transitions, will be suppressed and only quadrupole-allowed transitions forced by the transverse components of the field gradient will contribute. Instead of measuring the absorption spectra, the effects caused by the OAM of photons can be detected by a very sensitive method of monitoring the excitation spectra of emission. Such experiments may allow one to also get additional experimental information about the energy levels of centers, not available for spectroscopy with the usual photons.

The transitions with very low spontaneous emission probabilities (long spontaneous emission lifetimes), excited by twisted photons, can be used for bioimaging in the near-IR spectral range that will increase the signal-to-noise ratio not only in the presence of nanosecond autofluorescence of biotissues, but in the case of any parasitic luminescence of microsecond duration. In this way it is possible to reduce the adverse effect on healthy cells.

II. LAGUERRE-GAUSSIAN AND BESSEL-GAUSSIAN BEAMS WITH OAM

We consider the excitation of an atom (optical center in a crystal) by a ray of twisted photons, with OAM l propagating in the z direction. Two types of such beams are considered: (a) Laguerre-Gaussian and (b) Bessel-Gaussian beams. By using the polar coordinates ϕ, ρ, and z the operator of the vector potential of a Laguerre-Gaussian beam can be presented in the form $\hat{\hat{A}}_{lp} \equiv \vec{e}_0 \hat{A}_{lp}(\varphi,\rho,z)$, where $\vec{e}_0$ is the polarization (spin) of photons,

$$\hat{A}_{lp} \equiv \hat{A}_{lp}(\varphi,\rho,z) = \hat{A}_0 \Psi_{l,p}(\rho,\phi) e^{-ik_z z - \rho^2/2w_z^2}. \tag{1}$$

Here $\hat{A}_0$ is the operator of the vector-potential operator of the mode (k_z,l,p), $k_z = k\cos\vartheta$ is the longitudinal component of the wave vector of the photon,

$$\Psi_{l,p}^{\mathrm{LG}}(\rho,\phi) = w_z^{-1}\sqrt{\frac{p!}{\pi(|l|+p)!}}\left(\frac{\rho}{w_z}\right)^{|l|} L_p^{|l|}\left(\frac{\rho^2}{w_z^2}\right) \times e^{il\phi + ik_z\rho^2/2\left(z^2+z_R^2\right) + i\Phi_G(z)}, \tag{2}$$

$p \geqslant 0$ is an integer, $w_z = w_0\sqrt{1+(z/z_R)^2}/\sqrt{2}$ is the radius of the beam passing at the distance z from the optical center, $z_R = 2\pi w_0^2/\lambda$, $w_0 \gtrsim \lambda/\sqrt{2}\pi$ is the beam waist, and $\Phi_G(z)$ is the Gouy phase shift. The beam (2) is normalized: $\int \rho d\rho d\phi |\Psi_{l,p}^{\mathrm{LG}}(\rho\phi)|^2 = 1$.

In the case of the Laguerre-Gaussian beams, $L_p^{|l|}(x)$ are the generalized Laguerre polynomials. In the case of BGBs,

$$\Psi_{l,p}^{\mathrm{BG}}(\rho,\phi) = \sqrt{\frac{p}{\sqrt{\pi}\lambda w_0}} C_{l,p} J_l\left(\frac{p\rho}{\lambda}\right) e^{il\phi}, \tag{3}$$

where $J_l(x)$ is the Bessel function, $p = k_\rho \lambda = 2\pi \sin\vartheta$, $k_\rho = k\sin\vartheta$ is the radial component of the wave vector of photons, $\vartheta = \arctan(k_\rho/k_z)$, and $C_{l,p}$ is the normalization factor. In particular,

$$C_{1p} = \sqrt{\sqrt{\pi} w_0 \lambda/p}\left[e^{-p^2 w_0^2/2\lambda^2} I_1\left(p^2 w_0^2/2\lambda^2\right)\right]^{-1/2}. \tag{4}$$

In the case of $|w_0 p/\lambda| \gg 1$ one gets $C_{l,p} \approx 1$. For both LGBs and BGBs the larger p is, the higher the powers of ρ that give the main contribution. However, in BGBs, unlikely to LGBs, the parameter p has continuous values in the finite interval $|p| \leqslant 2\pi$. Below, p_{LG} and p_{BG} are used for the values of p for LGBs and BGBs, respectively. If $w_0 \gg \lambda$, then for $\rho \lesssim w_0$ one gets $|\Psi_{l,p}^{\mathrm{BG}}| \gg |\Psi_{l,p}^{\mathrm{LG}}|$; i.e., BGB is more focused than LGB. This is a consequence of an additional focusing due to the conical wave front of BGBs.

To find the intensities of new spectral lines, one needs to calculate the field gradient $\partial\Psi_{l,p}/\partial\rho$. In the case of a Laguerre-Gaussian beam it is convenient to perform this calculation by applying the relation between two-dimensional (2D) Hermite polynomials and Laguerre polynomials, derived in Ref. [20]. One gets (see the Appendix)

$$\frac{\partial\Psi_{|l|,p}^{\mathrm{LG}}}{\partial\rho} = \frac{(-1)^p}{2w_0}\Big(\sqrt{|l|+p}\,\Psi_{|l|-1,p}^{\mathrm{LG}} - \sqrt{p}\,\Psi_{|l|+1,p-1}^{\mathrm{LG}} + \sqrt{p+1}\,\Psi_{|l|-1,p+1}^{\mathrm{LG}} - \sqrt{|l|+p+1}\,\Psi_{|l|+1,p}^{\mathrm{LG}}\Big). \tag{5}$$

In the case of a Bessel-Gaussian beam, simple calculation gives

$$\frac{\partial\Psi^{\mathrm{BG}}_{|l|,p}}{\partial\rho}=\sqrt{\frac{p}{\sqrt{\pi}\lambda w_0}}C_{l,p}\left[\frac{|l|}{\rho}J_{|l|}\left(\frac{p\rho}{\lambda}\right)-\frac{p}{\lambda}J_{|l|+1}\left(\frac{p\rho}{\lambda}\right)\right]. \tag{6}$$

III. MATRIX ELEMENTS OF ABSORPTION

Here we are studying the absorption of twisted photons by an impurity atom/ion in a crystal. The interaction Hamiltonian of the electromagnetic field with an electron is equal to [21,22]

$$H_{\mathrm{int}}=-\frac{e}{2m_e c}(\hat{\vec{A}}\hat{\vec{p}}+\hat{\vec{p}}\hat{\vec{A}})+\frac{e^2}{m_e c^2}\hat{A}^2, \tag{7}$$

where e and m_e are the charge and mass of the electron (hole); $\hat{\vec{p}}$ is the operator of electron (hole) momentum. Note that the second term in the interaction Hamiltonian (7) can usually be neglected. If the system under consideration has more than one optical (valence) electron, then one should take a sum over all of them.

We suppose that the axis of the beam of twisted photons is displaced from the nucleus of the atom by some distance ρ_0 in the x direction. The nucleus of the atom/ion is situated at a point with $x=\rho_0$, $y=z=0$. Then the spherical coordinates of the optical electron in the atom are $x=r\sin(\vartheta)\cos(\varphi)$, $y=r\sin(\vartheta)\sin(\varphi)$, and $z=r\cos(\vartheta)$. We take into account that, due to the small size of an atom/ion a_0, the contribution to the matrix element of the electronic transition is given by terms with $x,y,\ z\sim a_0\ll w_0,\ \rho_0$. Therefore, the OAM-dependent phase factor $e^{i\phi l}\cong 1$ does not depend on the actual value of the coordinate of the optical electron in a center. Thus the centers, due to their smallness, do not "feel" the OAM (l) sign. However, they can feel the absolute value $|l|$ of the OAM. An exception arises for the centers located very close to the axis of the beam of twisted photons at a distance less than or comparable to the smallest size of the electronic wave function of the contributing electronic states. These centers can also feel the sign of the OAM. However, the number of such centers is small and their contribution is negligible.

To calculate the matrix element $\langle{}^4f|H_{\mathrm{int}}|{}^4f_0\rangle$ of the quadrupole-allowed transition $|{}^4f_0\rangle\rightarrow|{}^4f\rangle$ in the atom we expand the acting-to-the-center vector potential operator $\hat{A}$ in the series with respect to the coordinates of the electron in the atom and take into account up to the first-order terms, which are included. We get $A(\vec{r})=\hat{A}_0+\hat{A}_1 z+\hat{A}_2 x$, where $\hat{A}_0\equiv\hat{A}(0,\rho_0,0)$, $\hat{A}_1=ik\hat{A}_0\Psi_{lp}(\rho_0,0)$, and $A_2=\hat{A}_0\partial\Psi_{lp}(\rho,0)/\partial\rho|_{\rho=\rho_0}$ are the operators of the longitudinal and the transversal gradients of the field, respectively. The first term contributes to the electric dipole transition and does not contribute to the electric quadrupole transition under consideration. To find the contributions of last two terms we apply the identity

$$r_\alpha\hat{p}_\beta+\hat{p}_\beta r_\alpha\equiv r_\alpha\hat{p}_\beta+\hat{p}_\alpha r_\beta+\varepsilon_{\alpha\beta\gamma}\hat{L}_\gamma,$$

where α,β,γ are indices of Cartesian coordinates x,y,z; $r_{x,y,z}=x,y,z$; $\varepsilon_{\alpha\beta\gamma}$ is the Levi-Civita symbol; $\hat{\vec{L}}$ is the angular momentum operator (on repeated indices summation is carried out). The latter operator does not contribute to the electric quadrupole transitions (it contributes to magnetic dipole transitions). Also taking into account the relation $r_\alpha\hat{p}_\beta+\hat{p}_\alpha r_\beta=im_e[r_\alpha r_\beta,H_0]$ (the units $\hbar=1$ are used), and the ratios $H_0|f_0\rangle=E_{f_0}|f_0\rangle$ and $\langle f|H_0=E_f\langle f|$, where H_0 is the Hamiltonian of the electrons of the atom, and $[a,b]=ab-ba$ is the commutator of the operators a and b, the matrix element under consideration can be presented as the sum of following two terms:

$$M^{(1)}_{f_0,f}\simeq-\sqrt{\omega}(ke/c)\Psi_{l,p}(\rho_0,0)\langle f|(\vec{e}_0\vec{r})r\cdot\cos(\vartheta)|f_0\rangle, \tag{8}$$

$$M^{(2)}_{f_0,f}\simeq i\sqrt{\omega}\left(\frac{e}{cw_0}\right)\frac{\partial\Psi_{l,p}(\rho,0)}{\partial\rho}\bigg|_{\rho=\rho_0}\times\langle f|(\vec{e}_0\vec{r})r\cdot\sin(\vartheta)\cdot(\cos\varphi)|f_0\rangle, \tag{9}$$

where $\omega=E_f-E_{f_0}$ (the multiplier $\omega^{-1/2}$ comes from the operator $\hat{A}_0$). The matrix element $M^{(1)}_{f_0,f}$ describes the usual quadrupole transitions due to the longitudinal component of the field gradient (i.e., perpendicular to the wave front, it is presented also in the case of plane waves), while the matrix element $M^{(2)}_{f_0,f}$ describes the quadrupole transitions for photons with OAM due to the transversal component of the field gradient (parallel to the wave front). In Re^{3+} ions with several charged carriers (several f electrons or f holes) all these charge carriers contribute to the initial and final electronic states. For the matrix elements of such ions, one needs to take a sum over all these charge carriers.

IV. ABSORPTION IN A NANOCRYSTAL

The maximal gradient of the field is achieved at the axis of the beam with $|l|=1$. Therefore, the largest effect from the twist of photons is expected to be obtained for quadrupole transition by the optical centers situated close to the beam axis. Correspondingly, the maximal effect of the twist of such photons can be obtained for a nano- or microcrystal situated at small distances $\rho<w_0$ from the axis. For such crystals,

$$\left|\partial\Psi^{\mathrm{LG}}_{1,p}/\partial\rho\right|_{\rho=0}=w_0^{-2}\sqrt{p+1},$$

$$\left|\partial\Psi^{\mathrm{BG}}_{1,p}/\partial\rho\right|=C_{1,p}\sqrt{(p/\lambda)^3 w_0/\sqrt{\pi}}. \tag{10}$$

Using now Eqs. (8) and (9) we get the following equations for the squares of absolute value of matrix elements for the transitions caused by the longitudinal and the transversal components of the field gradient, respectively:

$$\left|M^{(1)}_{f_0,f}\right|^2\simeq\omega(ke/cw_0)^2|\Psi_{1,p}|^2|\langle f|(\vec{e}_0\vec{r})r\cos\vartheta|f_0\rangle|^2, \tag{11}$$

$$\left|M^{(2),\mathrm{LG}}_{f_0,f;1,p}\right|^2\simeq\omega\left(e/cw_0^2\right)^2(p+1)|\langle f|(\vec{e}_0\vec{r})r\times\sin(\vartheta)\cos(\varphi)|f_0\rangle|^2, \tag{12}$$

$$\left|M^{(2),\mathrm{BG}}_{f_0,f;1,p}\right|^2\simeq\frac{\omega e^2 p^2}{c^2\lambda^3 w_0\sqrt{\pi}}C^2_{1,p}|\langle f|(\vec{e}_0\vec{r})r\sin(\vartheta)\cos(\varphi)|f_0\rangle|^2, \tag{13}$$

where $|\Psi_{1,p}|^2=\alpha\rho_0^2$, $\alpha^{\mathrm{LG}}=1/\pi(p+1)w_0^4$, $\alpha^{\mathrm{BG}}=pC^2_{1.p}/\sqrt{\pi}\lambda^3 w_0$. Equations (11)–(13) determine the absorption probability. As expected, the light with large p has a large transverse field gradient and, thus, a stronger effect on the absorption caused by this gradient. Due to the zero value of the field Ψ_{1p} at the beam axis, the transitions caused by the longitudinal field gradient, as well as the forced dipole transitions between the ^4f levels, considered in Refs. [17–19], are absent in this case.

If $w_0 > \lambda(p_{\mathrm{LG}}+1)^{1/3}/p_{\mathrm{BG}}$ then $C_{1,p} \approx 1$, and the absorption probability of BGB is larger than that of LGB. To get the same probability, one needs to use a more tightly focused LGB. Another possibility is to use an LGB with large p. Note also the special case of a standing cylindrical wave as a limiting case of BGBs with the inclination angle $\vartheta \approx \pi/2$. In this case $\cos\vartheta \approx 0$ and the quadrupole transitions caused by the longitudinal component of the field gradient vanish. Thus the use of the Bessel beams with the angle $\vartheta \approx \pi/2$ should allow one to suppress the contribution from the competing quadrupole transitions caused by the longitudinal field gradient. We remind the reader that in this case, due to the zero value of the field at the beam axis, the contribution from the usually dominating forced dipole ^4f - ^4f transitions is also suppressed. Therefore, all lines in the absorption spectra of nano- or microcrystals placed close to the axis of such beams should be entirely due to the quadrupole transitions caused by the transverse field gradient of the twisted photons.

V. ABSORPTION IN A MACROCRYSTAL

To find the absorption of twisted photons by impurity centers in a macrocrystal, one must take into account that the centers (impurity atoms/ions) are situated at different distances ρ_0 from the beam axis. If the size of the crystal is macroscopic, then the centers become distributed over a large distance $\rho_0 \gg \lambda$, w_0 from the beam axis. Therefore, to find the total absorption, one should integrate the squares of the matrix elements given by Eqs. (8) and (9) over all the distances ρ_0 and all the angles ϕ_0. This gives

$$\langle |M^{(1)}_{f_0,f}|^2\rangle \simeq \omega(ke/c)^2|\langle f|(\vec{e}\vec{r})r\cos\vartheta|f_0\rangle|^2, \tag{14}$$

$$\langle |M^{(2)}_{f_0,f}|^2\rangle \simeq \omega(e/2cw_0)^2|\langle f|(\vec{e}\vec{r})r\sin(\vartheta)\cos(\varphi)|f_0\rangle|^2 W_{l,p}, \tag{15}$$

where the factor

$$W_{l,p} = \langle |\partial\Psi^{\mathrm{LG}}_{l,p}/\partial\rho|^2\rangle = \int_0^{2\pi} d\phi_0 \int_0^{\infty} \rho|\partial\Psi_{l,p}/\partial\rho|^2 d\rho \tag{16}$$

describes the dependence of the transition probability on the twist of photons. For LGB, inserting Eq. (5) here and taking into account that the functions $\Psi^{\mathrm{LG}}_{l,p}$ are orthogonal and normalized [20], we get

$$W^{\mathrm{LG}}_{l,p} = \tfrac{1}{2}(|l| + 2p + 1). \tag{17}$$

From Eq. (17) it follows that for the LGBs with large values of $|l|$ and p one can substantially increase the absorption by quadrupole-allowed transitions in macroscopic crystals. Thus, in principle there exists a possibility of increasing the probability of such quadrupole-allowed transitions by using the Laguerre-Gaussian beams with large radial and azimuthal quantum numbers. In the case of BGBs we get

$$W^{\mathrm{BG}}_{l,p} \approx p/\sqrt{\pi}, \tag{18}$$

where $p = 2\pi\sin\vartheta$. The largest intensity of new spectral lines for BGBs is obtained for the beams with $\vartheta \approx \pi/2$. The use of BGBs with the angle $\vartheta \approx \pi/2$ allows one also to suppress the contribution from the competing quadrupole transitions caused by the longitudinal field gradient $\propto k_z = 2\pi\sin\vartheta/\lambda$.

VI. ABSORPTION BY TRIVALENT RARE-EARTH IONS

To be specific, we are considering here the absorption of photons with OAM at ^4f - ^4f quadrupole transitions in the ^4f shell of the trivalent rare-earth ions in crystals. In these optical centers, the squared matrix elements of optical transitions can be calculated, e.g., by using the Judd-Ofelt theory [17–19]. According to this theory, the forced electrodipole transitions in Re^{3+} centers usually give the main contribution to the intensity of the spectral lines of ^4f - ^4f transitions (due to the presence of a weak non-central-symmetric field). An excitation by twisted photons of a nano- or microcrystal placed close to the beam axis allows one to suppress this contribution (due to the fact that the strengths of the field in such a beam are zero on the axis). In this case, the twisting of photons should have a remarkable effect in the absorption spectrum. Besides, there exist crystals with optical centers having inverse symmetry. In these crystals the forced dipole-allowed transitions are absent and only quadrupole-allowed transition exists. One can use such crystals also of macroscopic size for observing the effects of the photons' twist in the spectra.

In the spherical coordinates r,ϑ,φ the wave functions of the electrons (holes) in the ^4f shell, due to an almost perfect spherical symmetry of the effective potential energy of each electron, have a factorized form consisting of the product of radial and angular functions. The latter can be presented as linear combinations of spherical harmonics $Y^m_n(\vartheta,\varphi)$ (the states under consideration can be considered in the Russell-Saunders scheme). The weak crystal field causes a small ($\sim$100 cm^{-1}) Stark splitting of the levels with different m and mixes the m states with different m. In symmetric centers the states m are mixed with states $m \pm n$, where n is the order of the symmetry axis. The latter mixing leads to the following azimuthal angular dependence of the wave function of the ^4f state with the energy $^{(2S+1)}E_{J,m}$:

$$|^{(2S+1)}F^m_J(\varphi)\rangle \propto e^{im\varphi}[1 + \varsigma_{J,S,m}\cos(n\varphi)]. \tag{19}$$

Here $\varsigma_{J,S,m}$ is the small parameter describing the contribution of the effect of mixing the states by the S_4 field, and S is the full spin. As a result, the crystal field leads to the appearance of additional optical transitions. However, these additional transitions are rather weak and can be neglected here.

As an example, we consider the $^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition in cubic centers of Nd^{3+} in CaF_2 crystals with the energy $\approx$ 17 000 cm^{-1} (see, e.g., [23]). In both states (ground, $^4I_{9/2}$, and excited, $^4G_{5/2}$) the spin is 3/2 and it is antiparallel to the orbital momenta $L = 6$ and $L = 4$, respectively. We are considering the absorption of twisted circularly polarized photons with OAM $|l| = 1$. The spin (polarization) of the photon is equal to $s = \pm 1$, where $s = 1$ corresponds to the left-circularly

TABLE I. Crystal-field components of the $|^4I_{9/2}^{|m|}\rangle \rightarrow |^4G_{5/2}^{|m'|}\rangle$ transition in $CaF_2 : Nd^{3+}$.

$\lvert m \rvert$	5/2	3/2	1/2
9/2	tw_2		
7/2	**UN**	tw_2	
5/2	tw_0	**UN**	tw_2,
3/2	**UN**	tw_0	**UN**, tw_2
1/2	tw_2	tw_2	**UN**, tw_0

polarized light, and $s = -1$ to the right-circularly polarized light. Therefore, $(\vec{e}_0\vec{r}) = x + isy = r\sin\vartheta e^{is\varphi}$, which gives

$$\left\langle \left| M^{(1)}_{{}^4I_{9/2,m};{}^4G_{5/2,m'}} \right|^2 \right\rangle = (\pi\hbar\omega/4) m_e^2 k^2 w_0^2 \left| \langle {}^4G_{5/2,m'} | r^2 \times \sin(2\vartheta) e^{is\varphi} | {}^4I_{9/2,m} \rangle \right|^2, \tag{20}$$

$$\left\langle \left| M^{(2)}_{{}^4I_{9/2,m};{}^4G_{5/2,m'}} \right|^2 \right\rangle \simeq \omega (e/cw_0)^2 \left| \langle f | (\vec{e}\vec{r}) r^2 [1 + \cos(2\vartheta)] \times \cos(\varphi) e^{is\varphi} | f_0 \rangle \right|^2 W_{l,p}. \tag{21}$$

Now, by performing the integration over the azimuthal angle φ, one gets the selection rules for the absorption of circularly polarized photons with an OAM l. There are three groups of such transitions with the following $\Delta m = m' - m$:

$$(1)\ \Delta m = s = \pm 1, \quad (2)\ \Delta m = s + l/|l| = \pm 2, 0,$$
$$(3)\ \Delta m = s - l/|l| = 0, \mp 2.$$

These selection rules work differently for the centers with even and with odd number of ^4f electrons, i.e., for the centers with an integer m (diamagnetic centers) and a half integer m (paramagnetic centers). For diamagnetic centers, the energies of the Stark sublevels depend on m, while for paramagnetic centers the energies of the Stark sublevels depend only on $|m|$ (Kramers degeneracy). Correspondingly, the absorption spectrum of twisted photons in the case of a diamagnetic center should depend on the polarization of light. In the opposite, the absorption spectrum of twisted photons in the case of a paramagnetic center should not depend on the polarization of light (although it should depend on $|l|$ and p of the beam). However, in a strong external magnetic field the Kramers degeneracy will be removed. In this case, the absorption spectra produced by twisted photons in paramagnetic centers should also depend on the polarization of light.

The allowed transitions between the Stark components of the levels $|^4I_{9/2}^{|m|}\rangle \rightarrow |^4G_{5/2}^{|m'|}\rangle$ in an Nd^{3+} center for nontwisted (**UN**) and twisted photons ($tw_{0,2}$) are given in Table I (bold font corresponds to a more intense transition, the subscript stands for $|\Delta m|$).

Note that the transitions between several Stark components are allowed only for twisted photons. The Nd^{3+} ions in CaF_2 crystal are good emitters of light. Therefore, the corresponding transitions can be observed in the excitation spectra of the emission of CaF_2: the Nd^{3+} crystal at the $|^4I_{9/2}^{|m|}\rangle \rightarrow |^4G_{5/2}^{|m'|}\rangle$ transition. The symmetric crystal field plays a dual role here: (a) It leads to selection rules for the transitions, and (b) due to the Stark splitting of levels it distinguishes the spectral lines for twisted photons from other lines. As a result, the effect of OAM can be observed both in micro- and macrocrystals and without an external magnetic field. This allows one to study the effects caused by the OAM of photons by a very sensitive method of monitoring the excitation spectra of emission.

Similar effects are also possible in the Re^{3+}:$LiYF_4$ and other crystals with a similar structure where at least some of the centers have the inversion symmetry (point group S_4) that makes it possible to observe new spectral lines for these centers. Here again, the use of twisted photons may result in the onset of the transitions which are forbidden for nontwisted photons. Especially promising are the experiments with nano- or microsamples placed at the axis of the beam of twisted photons, while the usually dominating forced dipole transitions do not contribute there. The nano- or microsamples may be disordered or even amorphous. The use of BGBs with the angle $\vartheta \approx \pi/2$ should allow one also to suppress the contribution from the competing usual quadrupole transitions caused by the longitudinal field gradient.

VII. CONCLUSION

The presented results allow one to conclude that the use of twisted photons may result in the formation of absorption spectra that are different from those for the usual nontwisted photons. The difference exists for dipole-forbidden but quadrupole-allowed transitions as a consequence of the dependence of the latter transitions on the light field gradient. The absorption of twisted photons by an optical center depends on the absolute value $|l|$ of the azimuthal quantum number of twisted photons. The dependence on the sign of l is absent. It is a consequence of the small size of the electronic states of active centers as compared to the large spatial scale of the twist.

For the nanocrystals situated close to the beam axis new lines in the absorption spectra should appear for photons with $|l| = 1$. Note that in this case, due to the zero value of the field at the beam axis, the contribution from the usually dominating dipole ^4f - ^4f transitions is suppressed. The use of the Bessel beams with the angle $\vartheta \approx \pi/2$ should allow one also to suppress the contribution from the competing quadrupole transitions caused by the longitudinal field gradient. Therefore, all lines in the absorption spectra of nano- or microcrystals placed close to the axis of such beams should be entirely due to the quadrupole transitions caused by the transverse field gradient of the twisted photons.

In macroscopic crystals, the new lines in the absorption spectra appear for twisted photons with $|l| \neq 1$. This is the result of a finite field gradient in any paraxial beam with $|l| \neq 1$ at the finite distances $\rho \gtrsim w_0$ from the axis. Moreover, the absorption of twisted photons by macroscopic crystals increases with $|l|$ and p as $|l| + 2p + 1$. Consequently, the use of the Laguerre-Gaussian beams with large radial and azimuthal quantum numbers $|l|$ and p should allow one to increase the absorption caused by quadrupole-allowed transitions.

A promising object for the observation of the considered effects is the symmetric optical centers of three-valence rare-earth impurity ions in crystals, where the differences in the absorption spectra of nontwisted and twisted photons can appear for ^4f - ^4f quadrupole transitions in the ^4f shell of these ions. These centers are good emitters of light, which allows one to use the luminescence excitation spectra to observe the new spectral lines. For example, several transitions between different Stark components of quadrupole ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$ transitions in the cubic centers of Nd^{3+} in CaF_2 crystals are forbidden for usual nontwisted light excitation, but they can be observed through the appearance of new spectral lines under excitation by twisted photons. Note that these new lines should appear without any external magnetic field. When excited by twisted photons, the luminescence of such centers with their spontaneous emission lifetimes of tens of milliseconds can be used for bioimaging in the near-IR spectral range, which should increase the signal-to-noise ratio not only in the presence of nanosecond autofluorescence of biotissues, but in the case of any parasitic luminescence of microsecond duration as well. In this way it is also possible to reduce the adverse effect on healthy cells.

The differences in the absorption spectra of the usual and twisted photons must also exist for Re^{3+} optical centers in $LiYF_4$ and other crystals with a similar structure. The symmetric crystal field in such crystals leads to specific selection rules for transitions and, due to the Stark splitting, it gives a possibility to distinguish the spectral lines of twisted photons from other lines. In such a way, the use of twisted photons can allow one to get additional experimental information about the energy levels of centers, not available from the spectroscopy with the usual nontwisted light. Similar effects are also possible in the Re^{3+}:$LiYF_4$ and other crystals with a similar structure where at least some of the centers have the inversion symmetry (point group S_4) that makes it possible to observe new spectral lines for these centers. Here again, the use of twisted photons may result in the onset of transitions which are forbidden for nontwisted photons.

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APPENDIX

1. Laguerre-Gaussian beams

To find the intensities of the new spectral lines of the quadrupole transitions, one needs to calculate the transverse component of the beam field gradient. In the case of a Laguerre-Gaussian beam it is convenient go perform this calculation by applying the following relation between the 2D Hermite and Laguerre polynomials, derived in Ref. [20]. One gets (see Eqs. (2.6) and (3.6) in Ref. [20])

$$z^{n-n'} L_{n'}^{n-n'}(z\bar{z}) = (-1)^{n'} H_n(z) H_{n'}(\bar{z})/n'!, \quad n \geqslant n', \tag{A1}$$

where $z,\bar{z} \equiv \rho e^{\pm i\phi} \rightarrow (x \pm iy)/\sqrt{2}$. Multiplying both sides of this equation by $e^{-z\bar{z}/2}$ we find that Eq. (A1) reduces (up to the sign) to the eigenfunction of a two-dimensional harmonic oscillator with the given momentum $l = n - n'$ and with the radial quantum number $p = \min(n,n')$. For $l \geqslant 0$ the corresponding relation gets the form

$$\left|\Psi_p^l\right\rangle = (-1)^p \left|\psi_{l+p}^{(+)}\right\rangle \left|\psi_p^{(-)}\right\rangle, \tag{A2}$$

where $|\psi_n^{(\pm)}\rangle = \sqrt{1/n!}\,(\hat{a}_\pm^+)^n |\psi_0^{(\pm)}\rangle$ is the eigenstate number n of the Hamiltonian of the dimensionless harmonic oscillator with the corresponding Hamiltonian,

$$H_\pm = \hat{a}_\pm^+ \hat{a}_\pm + 1/2, \tag{A3}$$

where $\hat{a}_\pm^+ = (\hat{a}_x^+ \pm i\hat{a}_y^+)/\sqrt{2}$ and $\hat{a}_\pm = (\hat{a}_x \pm i\hat{a}_y)/\sqrt{2}$ are the creation and destruction operators of the quanta with positive (+) and negative (−) rotational momentum; $\hat{a}_x = (x/w_0 + w_0\partial/\partial x)/\sqrt{2}$ is the destruction operator of the one-dimensional oscillator with the coordinate x/w_0. In a similar way, the operator $\hat{a}_y$ and the operators $\hat{a}_x^+$ and $\hat{a}_y^+$ are defined. From these equations it follows that

$$\partial/\partial x = (\hat{a}_+ + \hat{a}_- - \hat{a}_-^+ - \hat{a}_+^+)/2w_0, \tag{A4}$$

$$\begin{aligned}\partial\Psi_p^{|l|}/\partial x = {} & [(-1)^p/2w_z]\big(\sqrt{|l|+p}\,\Psi_p^{|l|-1} - \sqrt{p}\,\Psi_{p-1}^{|l|+1} \\ & + \sqrt{p+1}\,\Psi_{p+1}^{|l|-1} - \sqrt{|l|+p+1}\,\Psi_p^{|l|+1}\big).\end{aligned} \tag{A5}$$

2. Hermite-Gaussian beams

The effect of the transverse gradient of a light beam can be observed also for beams without OAM, e.g., for a Hermite-Gaussian beam:

$$\Psi_{n,n'}(x,y) = H_n(x/w_x) H_{n'}(x/w_y). \tag{A6}$$

To suppress the dipole transitions in microcrystals placed close to the beam axis one needs to use a beam with zero intensity close to the axis. Therefore one needs to use a beam with at least one quantum number, n or n', to be odd. To calculate the field gradient at the origin we take into account the relation $H'_{2j+1}(0) = (-1)^n 2(2j+1)!/j!$. We get that the probability of absorption by nano- or microcrystals situated close to the beam's axis for such a beam has the factor $w_n + w_{n'}$, where the nonzero values of w_n are (for $n = 2j + 1$)

$$w_{2j+1} = \frac{(2j+1)!}{\sqrt{\pi}(2^j j!)^2}. \tag{A7}$$

This factor is smaller than the corresponding factor $(1 + p)$ for LGB with $p = \min(n,n')$ and $l = n - n'$. For macroscopic crystals the field gradient also in the case of the Hermite-Gaussian beams gets nonzero values for a great majority of centers. A simple calculation shows that the probability factors for these beams are the same as for the LGBs with $p = \min(n,n')$ and $l = n - n'$.

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