Fast qubits of optical frequencies on the rare-earth ions in fluoride crystals and color centers in diamond

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Fluoride crystals doped with rare-earth ions (REI) and pair centers in diamond for fast (10^{-9}s) quantum computers (QFC) are proposed. As specific systems for REI doping, we propose Ca_{1-x}Sr_xF_2 crystals and their analogues. The 4f-states with different total orbital angular momenta of these ions serve as two-level systems (qubits). Suitable REIs are proposed as well. It is established that the pair SiV centers in diamond are promising systems for fast optical quantum computers operating at elevated temperatures.

**Keywords:** CNOT gates, fast qubits of optical frequencies, rare-earth ions, SiV and GeV centers in diamond.

I. INTRODUCTION

We discuss the possibility of creation fast (GHz) optical quantum computers (OQC) using mixed nanocrystals doped with rare-earth ions (REI) and diamond with pair SiV and GeV optical centers (OCs). The qubits in these systems have optical frequencies and can operate at high (GHz) speed.

Recently we have found [1] that crystals Ca_{1-x}Sr_xF_2 and their analogs doped with REIs can be considered as promising candidates for the role of fast OQC. In the specified crystals one must use REIs that have 4f states with small and large diagonal elements of the Judd-Ofelt matrix U^{(2)}; the states with a small elements can be used for qubits, and the states with large elements can be used for implementing CNOT and other conditional operations.

In a number of previous studies of the use of crystals doped with REIs as quantum computers, the authors considered the use of hyperfine levels as qubits (see [2] and the references therein). One-qubit operations with such qubits require two optical π-pulses. These pulses must have a small spectral width, much less than the qubit frequency. Therefore, such qubits can operate with millisecond or longer sampling time.

However, if to use REIs qubits with optical frequencies, then the spectral width of the light pulses will be incomparably less than the frequencies of the qubits. In this case, the light pulses will be much shorter than in the case of qubits with hyperfine levels. The weak interaction of 4f-electrons with surroundings allows to have qubits with a long coherence time. In this case one-qubit gate operations can be performed using single light pulses; conditional gate operations can be performed using multiple optical pulses and a Stark blockade [1].

This article also draws attention to the fact that the pair centers of REIs and of other ions can also be used as fast optical frequency qubits for OQCs. Here we take into account that such centers have cooperative excited states: dark and bright. Dark states can be used for qubits, and bright states are suitable for implementing a conditional gate operations. Pair SiV and GeV centers in diamond are especially promising for the development of fast OQCs. The advantage of such a OQC is that it can operate at elevated (possibly nitrogen) temperature.

II. MATERIALS AND METHODS

A. Mixed fluoride crystals doped with REIs

The mixed Ca_{1-x}Sr_xF_2 crystals doped with REI has a large inhomogeneous width Γ_{inh} ≈ THz and small homogeneous width Γ_h ≲ MHz of zero phonon lines (ZPLs) in their optical spectra. This is of great importance for the use of laser pulses with a spectral width τ ≈ ns requires the use of laser pulses with a spectral width Γ_L ≈ GHz. The condition Γ_{inh} ≫ Γ_L ensures that a large number of qubits can be addressed individually using laser pulses with different frequencies.

To perform the CNOT gate operation, it is necessary to violate the excitation of the target qubit by changing the state of the control qubit. If the used states interact so strongly that the frequency shift δ at this change exceeds Γ_L, then this condition is fulfilled. Previously the exchange dipole-dipole interaction was considered as the main interaction responsible for this phenomenon. Therefore, the term "dipole blockade" was used to denote it [2]. However, we have found that, due to small oscillator strength of 4f−4f transitions, for small and intermediate distances the strongest interaction is the static (Stark) quadrupole-quadrupole interaction (see [1]). Therefore, here we use the term Stark blockade. We also found that the Stark blockade is determined by the diagonal matrix elements of the Judd-Ofelt matrix U^{(2)}. These matrix elements have extremely scattered values, which differ by many orders of magnitude. This allows to use the 4f levels with small diagonal elements of the matrix U^{(2)} as qubit levels |0⟩ and |1⟩; and the 4f levels with large di-
agonal elements of the matrix \( U^{(2)} \) as auxiliary levels \( |1'\rangle \) to implement conditional gate operations [1].

**B. Pair centers in diamond and fluoride crystals**

Pair REI centers in fluoride crystals and others can also be used as fast optical frequency qubits for OQCs. This is due to the fact that such centers have cooperative excited states: dark and bright. Dark states can be used for the qubits themselves, and bright states are suitable for conditional gate operations. Paired SiV and GeV centers in diamond are especially promising for fast OQCs, because, due to the very high Debye frequency, they can operate at elevated temperatures.

**C. Laser excitation**

The OQCs with electronic states of impurity centers in crystals can operate using a sequence of resonant light \( \pi \)-pulses. The intensity of such a pulse is [1]

\[
I = 4\pi^2 k_0^2 \frac{k^3}{3\gamma_0 Z},
\]

where \( k = \omega n/c \) is the wave number of light with frequency \( \omega \), \( n \) is the refractive index, \( Z = 376.7 \) ohm is the impedance of free space. For \( k = 20000 \) \( \text{cm}^{-1} \), \( \gamma_0 = 1.5 \) ns and \( \Gamma_L = 10^9 \) sec\(^{-1} \) the intensity of the light of the pulse is \( I \sim 10^6 \) W/cm\(^2\). The energy of the pulse \( E_p = IS/\Gamma_L \) for the beam crosssection \( S = 10^{-7} \) cm\(^2\) is \( 10^{-14} \) J. For REIs as qubits, the pulse energy should be about four orders of magnitude higher due to the rather low rate of radiative decay \( \gamma_0 \) [1]. The corresponding field strength \( \sim 3 \times 10^4 \) V/cm, although high, is still four orders of magnitude less than the interatomic field strength, which means that it does not lead to radiation damage to the crystal.

**III. RESULTS**

**A. Rare earth ions and their \( ^4f \)-states suitable for fast OQCs**

For OQC, \( \text{Pr}^{3+} \) ions can be used with the ground state \( ^3H_4 \) as the auxiliary states and the states \( ^1G_4 \) (in \( \text{Pr}^{3+} : \text{YLiF}_3, \tau = 14 \mu s \), see [3]) and \( ^3P_0 \) (in \( \text{Pr}^{3+} : \text{LaF}_3, \tau = 55 \mu s \), see [4]) as qubit states (Figure [1]). Optical transition between all these levels is reasonably allowed. The calculations begin with preparation of states \( |0\rangle \) using the \( \pi \)-pulse excitation of the \( ^3H_4 \rightarrow ^1G_4 \) transition.

In figures 1-3, one can see the scheme of CNOT operation for the \( \text{Pr}^{3+}, \text{Er}^{3+}, \) and \( \text{Tm}^{3+} \) ions in mixed doped microcrystals with large inhomogeneous broadening. The arrows indicate the excitation by \( \pi \)-light pulses, the numbers denote the pulse sequence. The circles indicate the initially occupied levels of the control qubits. \( \delta_{\text{shift}} \) is a shift of the auxiliary level in the target qubit by changing the state of the control ones. \( \delta_i \) is a shift of the energy of the target optical qubit level relative to the control one. The squares of the reduced matrix elements \( U^{(k)} \) of the inter-level transitions are in brackets. The intra-level \( U^{(k)} \) values are near the corresponding levels.

The relative position of the levels can be different. The \( \text{Er}^{3+} \) ion ground state \( ^4I_{15/2} \) suits for the auxiliary state and states \( ^4I_{9/2} \) (in \( \text{Er}^{3+} : \text{LaF}_3, \tau = 133 \mu s \), see [2]) and \( ^4S_{3/2} \) (in \( \text{Er}^{3+} : \text{LaF}_3, \tau = 923 \mu s \), [4]) as qubit levels.

The \( \text{Tm}^{3+} \) ion provides several choices for the qubit

**Pr\(^{3+}\)**

![Diagram of Pr\(^{3+}\)](image)

**Er\(^{3+}\)**

![Diagram of Er\(^{3+}\)](image)

**Tm\(^{3+}\)**

![Diagram of Tm\(^{3+}\)](image)
and auxiliary level. For example, the lowest level $|3H_e\rangle$ of the $Tm^{3+}$ ion has a rather large diagonal element of matrix $U^{(2)} = 1.25$ (Figure 3), and it can be used as an auxiliary level $|1\rangle$. In this case, levels $|0\rangle = |3F_{4}\rangle$ ($E = 5619 \text{ cm}^{-1}$, lifetime $\tau = 18.05 \text{ ms}$ in $Tm^{3+}$: LiYF 4, [1]) and $|1\rangle = |1D_{2}\rangle$ ($E = 27830 \text{ cm}^{-1}$, lifetime $\tau = 70\mu\text{s}$ in $Tm^{3+}$: LiYF 4, [8]) have much smaller diagonal element of matrix $U^{(2)}$ and can be used as qubit levels. Another option (Figure 3) is that the initial state $|0\rangle$ is prepared by applying a pulse with frequency of $12518 \text{ cm}^{-1}$ to the allowed transition $|g\rangle \rightarrow |0\rangle$ from the ground state $|g\rangle = |3H_e\rangle$. In the case of the $Tm^{3+}$ ion, high energy level $|1I_6\rangle$ ($E = 34684 \text{ cm}^{-1}$, lifetime $\tau = 300\mu\text{s}$ in $Tm^{3+}$: $\beta$-NaYF 4, see [7]) has especially large diagonal element of matrix $U^{(2)}$ ($|U^{(2)}|_{1I_6I_6}|^2 = 4.88$), and it can be used also as auxiliary level. Then one can use the levels $|0\rangle = |3H_{1}\rangle$ and $|1\rangle = |1D_{2}\rangle$ as qubit levels. Very large value of $|U^{(2)}|_{1I_6I_6}|^2$ suggests that this scheme may be used for implementation of CNOT gate in case of large mean distance between $Tm^{3+}$ ions.

B. Pair centers

1. Electronic states of pair OCs

Among the very wide variety of crystals doped with various impurities, one can find many such crystals in the optical spectra of which there are strong zero-phonon lines with small homogeneous and large inhomogeneous width. Such crystals can be of interest as working elements of optical quantum computers, although individual centers may not have both strongly and weakly interacting states required for one-qubit and two-qubit gate operations. Indeed, this disadvantage of single centers can be overcome if a pair of such centers located nearby is used for a qubit. It is taken into account that the paired center has cooperative excited states: dark and light. Dark states interact weakly and can be used for qubits. The dipole-dipole exchange interaction of bright states is strong (compared to dark states), so they are suitable for the implementation of conditional gate operations.

The energies and the wave functions of the stationary states of the pair OC consisting of two almost identical centers are:

$$E_0 \simeq E - \Delta, \quad |0\rangle \simeq 2^{-1/2}(1 - \varepsilon/\Delta)\Psi_1(x_1)\Psi_2(x_2)$$

$$- (1 + \varepsilon/\Delta)\Psi_2(x_1)\Psi_1(x_2),$$

$$E_1 = 0, \quad |1\rangle = \Psi_1(x_1)\Psi_1(x_2),$$

$$E_1' \simeq E + \Delta, \quad |1'\rangle \simeq 2^{-1/2}(1 - \varepsilon/\Delta)\Psi_1(x_1)\Psi_2(x_2)$$

$$+ (1 + \varepsilon/\Delta)\Psi_2(x_1)\Psi_1(x_2),$$

$$E_2 = 2E, \quad |2\rangle = \Psi_2(x_1)\Psi_2(x_2).$$

Here $E_0 \pm \varepsilon$ are the differences in the energy of the excited ($\Psi_2$) and ground ($\Psi_1$) states of the single centers forming the pair OC center, $\Delta$ is the exchange interaction in the pair OC assumed that half of the energy difference $\varepsilon$ between the levels of the single centers forming a pair OC is very small as compared to the exchange interaction energy ($\varepsilon \ll \Delta$). In this case $|0\rangle$ is the metastable (dark) state, while $|1'\rangle$ is the radiative (bright) state with $(\Delta/\varepsilon)^2$ times larger oscillator strength of the dipole transition to the ground state $|1\rangle$ than of the dark state and twice large oscillator strength than the oscillator strength of the single center. Due to the large oscillator strength, the exchange dipole-dipole interaction of two pair OCs in the states $|1'\rangle$ is strong. Therefore, the dipole blockade in these states is also strong [8], and these states can be used to implement the CNOT and other conditional gate operations. On the contrary, two pair OCs in a dark state $|0\rangle$ interact very weakly. Therefore, these states can be used as the states of qubits.

2. SiV and GeV pair centers in diamond

Especially promising are pair SiV$^-$ and GeV$^-$ centers in diamond due to large oscillator strength of the optical transitions in the centers, high quantum yield of these transitions and very high Debye frequency of diamond allowing to work at elevated temperature. Other important advantages of these centers are that, due to very large oscillator strength of the optical transitions, it is possible to use relatively weak laser pulses and crystals having a low concentration of OQDs $\sim 10^{-4} - 10^{-6}$.

The single SiV and GeV OCs have half a spin. Therefore, pair SiV of GeV OC can be in the singlet and triplet states. However, due to singlet-triplet relaxation, only excited states with lower energies can be of interest. The energy level diagram of a pair OC consisting of two half-spin OCs is given in Figure 3 in [9].

A schematic diagram of the CNOT gate operation using paired centers is shown in Figure 4.

Note that recently pair NV centers in diamond, similar to pair SiV and GeV centers, were investigated in
3. Pair centers of rare earth ions: Nd$^{3+}$ in CaF$_2$

Pair optical centers of REIs are also promising systems for OQCs due to rather weak interaction with an environment and a large number of electronic states in a center with different properties, which allow to fulfill corresponding criteria (DiVincenzo’s criteria); see, for example [2]. Additional opportunities arise if we use the pair REI OCs.

Compared to the SiV and GeV OCs in diamond, the REI OCs have a disadvantage – optical transitions in these centers have a much lower oscillator strength and, therefore, these centers interact much weaker with each other. However, this weakening of the interaction can be compensated for by the possibility of using a high REIs concentration. Moreover, if doped crystals with divalent ions as charge compensators. Such centers have a large static dipole moment and interact quite strongly. This allows a large number of single centers to be converted into pair ones, for example, using heat treatment.

To make a microcrystal to work as an OQC instance, we must find the frequencies of N $\sim$ 10$^2$ closely spaced pair OCs. This can be done, using the spectral hole burning and gain (anti-hole) saturation method, see [1].

IV. DISCUSSION

Here we indicated that optical centers of rare-earth ions (REIs) in fluoride crystals and paired centers in these crystals and in diamond can be used to create fast (with sampling time 10$^{-9}$s) optical quantum computers (OQC). As specific crystals for REI doping, we propose $Ca_{1-x}SrxF_2$ crystals and their analogues. The $4f$-states with different total orbital angular moments of REIs in these crystals serve as two-level systems (qubits).

We have found that the $4f$ levels with small diagonal elements of the matrix $U$ can be used as qubit levels $|0\rangle$ and $|1\rangle$; and the $4f$ levels with large diagonal elements of the matrix $U$ can be used as auxiliary levels $|1'\rangle$ to implement conditional gate operations. A few specific rare earth ions and the corresponding $4f$ levels of these ions have been proposed for OQC (see Figs. 1-3).

It was also found that, on the whole, crystals with strong ZPLs with a small homogeneous and large inhomogeneous width in optical spectra may be of interest as possible candidates for qubits of OQCs, even if individual centers do not have both strongly and weakly interacting states necessary for one-qubit and two-qubit gate operations. The reason is that this disadvantage of such single centers can be overcome by using a pair of such centers located nearby for the qubits. It is taken into account that the paired centers have cooperative excited states: dark and bright. Dark states can be used for qubits, and bright states are suitable for implementing a conditional gate operations.

It is also found that the SiV and GeV pair OCs in diamond and the REI pair OCs in fluoride-type crystals are promising systems for use as optical frequency qubits in fast OQSs. In diamond with low concentration of SiV and/or GeV OCs, for the successful use of paired OCs for fast OCs, a significant part of the centers must be converted to paired OCs. If all single centers will be converted to pair OCs then the required minimum concentration will be $c \sim (a/R_0)^3 \sim 10^{-5}$.

Pair OCs of Nd$^{3+}$ ions in CaF$_2$ can serve as an example of pair REI OCs. Let us consider such a crystal with concentration $c \sim 0.01$ of Nd$^{3+}$ centers and assume that the spectral width of laser $\Gamma_L \sim 0.1$ GHz, inhomogeneous width of ZPL $\Gamma_{inh} \sim$ THz and the homogeneous width of ZPL is $\Gamma_h \lesssim \Gamma_L$. In this case the concentration of OCs with the same (up to $\Gamma_L$) frequency is $c\Gamma_L/\Gamma_{inh}$ giving $R_0 \sim 100\alpha$ for the mean size of the microcrystal working as a separate OQC instance.

Consider an ensemble of N=50 REIs closest to the excited one, which can act as an OQC instance. The mean size of this ensemble is $(N/c)^{1/3}a \sim 17a$. According to [1], the strongest interaction between REIs in this ensemble of ions is the quadrupole-quadrupole, giving $\delta \sim$ GHz. This interaction exceeds $\Gamma_L$. Therefore, in this case, fast CNOT gate operations can indeed be successfully performed for all N=50 pairs working as qubits.

V. SUMMARY

It was found that optical centers of rare-earth ions (REIs) in fluoride crystals can be used to create fast (with sampling time 10$^{-9}$s) optical quantum computers (OQC). It was also found that pair optical centers in crystals with strong ZPL with large inhomogeneous and small homogeneous width in their spectrum are also promising systems for fast optical quantum computers: the dark states of the pair centers can be used as states of the qubits, while the bright states are suitable for CNOT and other conditional gate operations. A scheme of CNOT gate operation for pair centers is proposed, including the required sequence of laser pulses.

Of particular interest for OQCs are SiV and GeV pair optical centers in diamond, since these OCs can operate as qubits at elevated temperatures. Pair optical centers of REIs in fluoride-type crystals are found to be also good candidates for OQCs; their use makes it possible to significantly expand the possibilities of choosing suitable REIs.

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[1] Hizhnyakov, V.; Boltrushko, V.; Kaasik, H.; Orlovskii, Yu. Rare earth ions doped mixed crystals for fast quantum computers with optical frequency qubits. *Optics Communications* **485**, 126693 (2021).

[2] Wesenberg, J.H.; Mølmer, K.; Rippe, L.; Kröll, S. Scalable designs for quantum computing with rare-earth-ion-doped crystals. *Physical Review A* **75**, pp. 012304-1–012304-7 (2007).

[3] Basiev, T.T.; Orlovskii, Yu.V.; Pukhov, K.K.; Sigachev, V.B.; Doroshenko, M.E.; Vorob’ev, I.N. Multiphonon relaxation rates measurements and theoretical calculations in the frame of non-linear and non-Coulomb model of a rare-earth ion-ligand interaction. *Journal of Luminescence* **68**, pp. 241–253 (1996).

[4] Brown, M.R.; Whiting, J.S.S.; Shand, W.A. Ion-Ion Interactions in Rare-Earth-Doped LaF₃. *The Journal of Chemical Physics* **43**, pp. 1–9 (1965).

[5] Okamoto, E.; Sekita, M.; Masui, H. Energy transfer between Er³⁺ ions in LaF₃. *Physical Review B* **11**, pp. 5103–5111 (1975).

[6] Walsh, B.M.; Barnes, N.P.; Di Bartolo, B. Branching ratios, cross sections, and radiative lifetimes of rare earth ions in solids: Application to Tm³⁺ and Ho³⁺ ions in LiYF₄. *J.Appl.Phys.* **83**, pp. 2772–2787 (1998).

[7] Shi, F.; Wang, J.; Zhang, D.; Qin, G.; Qin, W. Greatly enhanced size-tunable ultraviolet upconversion luminescence of monodisperse β-NaYF₄ : Yb, Tm nanocrystals. *Journal of Materials Chemistry* **21**(35), pp. 13413–13421 (2011).

[8] Lukin, M.D.; Fleischhauer, M.; Cote, R.; Duan, L.M.; Jaksch, D.; Cirac, J.I.; and Zoller, P. Dipole blockade and quantum information processing in mesoscopic atomic ensembles, *Physical Review Letters* **87**, pp. 037901-1 – 037901-4 (2001).

[9] Orlovskii, Yu.V.; Gross, H.; Vinogradova, E.E.; Boltrushko, V.; Hizhnyakov, V. Spectroscopic evidence of cooperative (entangled) quantum states of Nd³⁺ ion pairs in Nd³⁺ : LaF₃ crystal. *Journal of Luminescence* **219**, pp. 116920–116920 (2020).

[10] Chou, J.-P.; Bodrog, Z; Gali, A. First-principles study of charge diffusion between proximate solid-state qubits and its implications on sensor applications. *Phys.Rev.Lett.* **120**, pp. 136401-1–136401-5 (2018).