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# Ultrafast Quantum Relaxation Dynamics of Magnetically Ordered Systems with Spin Crossover in an Excited State under a Sudden Perturbation

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A theoretical model based on the relaxation equation for the density matrix has been proposed to describe the ultrafast time dynamics of magnetically ordered systems with spin crossover in an excited state under a sudden perturbation. Oscillations of the magnetization, the population of the high-spin state, and the generation of local vibrons at a transition of the system from the light-excited Franck–Condon low-spin state to the high-spin ground state.

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1. A new field called ultrafast magnetism has appeared and developed in the last decade in condensed matter physics [1–5]. Intense ultrashort laser pulses can excite spin dynamics in magnetic materials, which is of great fundamental and applied interest. The main experimental method in this field is the pump–probe technique [6, 7]. Depending on the properties of a magnetic medium, the pump pulse results in ultrafast demagnetization or magnetization reversal of a sample or in the excitation of the precession of the magnetization. The exchange interaction can change because of the interaction with light [8].

Systems with spin crossover [9–11], which can exist in a crystal phase and in the form of complex-molecular aperiodic compounds, are among nonstandard systems interesting for the study of ultrafast magnetic switching. In particular, the authors of [12] studied the light induced spin state trapping (LIESST) effect in the Fe(phen)<sub>2</sub>(NCS)<sub>2</sub> compound [9, 10] by X-ray absorption near edge spectroscopy (XANES) and time-resolved optical spectroscopy. They detected local deformations of ligands and the excitation of various vibron modes at the transition of the Fe<sup>2+</sup> ion from a low-spin (LS) to high-spin (HS) state. Iron oxides with the Fe<sup>3+</sup> and Fe<sup>2+</sup> ions with the HS ground state, where the spin crossover to the LS state occurs at high pressures, constitute another important class of compounds with spin crossover [13].

In this work, we consider the ultrafast quantum relaxation dynamics of the photoexcited state with the spin different from the spin of the ground state (which can be called the dynamic spin crossover) in magnetically ordered materials with allowance for the spin–orbit coupling between the HS and LS states and the electron–vibration interaction beyond the adiabatic approximation. A feature of magnetically ordered systems is the interatomic exchange interaction, which, together with the elastic interaction, is responsible for cooperative phenomena near spin crossover.

2. For definiteness, we consider only the case of  $d^6$  ions (FeO and Mg<sub>1-x</sub>Fe<sub>x</sub>O), for which  $S_{\text{HS}} = S = 2$  and  $S_{\text{LS}} = 0$ . To describe the possible coexistence of different cation terms, spin variables are inappropriate because they act only in the subspace of spin sublevels of a given spin. In this case, it is more adequate to use Hubbard operators that can be constructed on the basis of eigenstates of a cation including several terms. In this case, Hubbard  $X$  operators are constructed in terms of HS states with different spin projections  $|\sigma\rangle$ ,  $\sigma = -S, -S + 1, \dots, +S$  and the singlet LS state  $|s\rangle$ . The effective Hamiltonian for the description of the effect of the exchange interaction between HS states including the vibron and spin–orbit coupling can be written in the form

$$\hat{H}_{\text{eff}} = \hat{H}^{(S)} + \hat{H}^{(e,q)} + \hat{H}^{(SO)}. \quad (1)$$

Here,

$$\hat{H}^{(S)} = \frac{1}{2}J \sum_{\langle i,j \rangle} \left( \hat{S}_i \hat{S}_j - \frac{1}{4} \hat{n}_i \hat{n}_j \right) + \Delta_S \sum_i X_i^{s,s}, \quad (2)$$

where  $J$  is the interatomic exchange interaction and the spin energy gap  $\Delta_S = E_{LS} - E_{HS}$ , i.e., the difference between the energies  $E_{LS}$  and  $E_{HS}$  of the electron configurations of the LS and HS states, is determined by the competition of the intra-atomic Hund exchange interaction with the crystal field  $10Dq$ . We consider only the case of the high-spin ground state,  $E_{LS} > E_{HS}$ . The spin operators for  $S = 2$  in the Hubbard operator representation have the form [14]

$$\hat{S}_i^+ = 2X_i^{-1,-2} + \sqrt{6}X_i^{0,-1} + \sqrt{6}X_i^{+1,0} + 2X_i^{+2,+1}, \quad \hat{S}_i^- = 2X_i^{-2,-1} + \sqrt{6}X_i^{-1,0} + \sqrt{6}X_i^{0,+1} + 2X_i^{+1,+2}, \quad \text{and} \quad \hat{S}_i^z = 2X_i^{-2,-2} + X_i^{-1,-1} + X_i^{+1,+1} + 2X_i^{+2,+2};$$

the particle number operator at the  $i$ th site is  $\hat{n}_i = 6 \sum_{\sigma=-S}^{+S} X_i^{\sigma,\sigma} + 6X_i^{s,s}$ .

The condition of the completeness for Hubbard  $X$  operators has the form  $\sum_{\sigma=-S}^{+S} X^{\sigma,\sigma} + X^{s,s} = 1$ , and the

average number of electrons for a  $d^6$  ion is  $\langle \hat{n}_i \rangle = 6$ . The derivation of the effective Hamiltonian (2) from the microscopic multiband  $p-d$  model using the projection operator technique within the multielectron LDA + GTB method [15] can be found in [16].

The second term in Eq. (1) contains the energy of local totally symmetric vibrations of the cation–anion complex (which we consider as a unit cell and below will be called the SK complex, taking into account the possibility of occupation of either the HS or the LS at the spin crossover), electron–vibration (vibron) coupling [17, 18], and elastic interaction of cations at neighboring lattice sites, and describes the change in the volume of the system under the variation of temperature:

$$\hat{H}^{(e,q)} = \sum_i \left( \frac{1}{2}k\hat{q}_i^2 + \frac{\hat{p}_i^2}{2M} \right) - \sum_i (g_1\hat{q}_i + g_2\hat{q}_i^2) \left( -X_i^{s,s} + \sum_{\sigma=-S}^{+S} X_i^{\sigma,\sigma} \right) - \frac{1}{2}V_q \sum_{\langle i,j \rangle} \hat{q}_i \hat{q}_j. \quad (3)$$

Here,  $g_1$  and  $g_2$  are the electron–vibration coupling constants,  $k$  is the elastic coupling constant,  $\hat{q}$  is the normal coordinate operator corresponding to the breather vibrational mode of ligands,  $\hat{p}$  is the conjugate momentum operator,  $V_q$  is the elastic intermolecular coupling constant, and  $M$  is the effective mass of the oscillator. Since the ionic radii of cations in the LS and HS states are significantly different (by about 10%), not only linear terms but also terms quadratic in  $\hat{q}$  should be taken into account in the electron–vibration coupling. The elastic coupling constants in the LS

and HS states are  $k_{LS} = k + 2g_2$  and  $k_{HS} = k - 2g_2$ , respectively. Because of anharmonicity in the electron–phonon coupling, the frequencies of local vibrations in the HS and LS states are different:  $\omega_{HS} = \sqrt{(k - 2g_2)/M}$  and  $\omega_{LS} = \sqrt{(k + 2g_2)/M}$ . For the chosen parameters presented below,  $\omega_{HS} = 0.045$  eV and  $\omega_{LS} = 0.055$  eV.

The third term in Eq. (1) has the form

$$\hat{H}^{(SO)} = J_x \sum_i \sum_{\sigma=-S}^{+S} (X_i^{s,\sigma} + X_i^{\sigma,s}) \quad (4)$$

and mixes the HS and LS states because of the spin–orbit coupling [19].

When all interactions inside the spin crossover complex are taken into account exactly and the mean field approximation is used for the elastic and exchange intercell interaction, the Hamiltonian (1) has the form

$$\begin{aligned} \hat{H}_{\text{eff}} = & -B \sum_i \hat{S}_i^z + \Delta_S \sum_i X_i^{s,s} \\ & + \sum_i \left( \frac{1}{2}k\hat{q}_i^2 + \frac{\hat{p}_i^2}{2M} \right) - \sum_i (g_1\hat{q}_i + g_2\hat{q}_i^2) \\ & \times \left( -X_i^{s,s} + \sum_{\sigma=-S}^{+S} X_i^{\sigma,\sigma} \right) - V_q z \langle \hat{q} \rangle \sum_i \hat{q}_i \\ & + J_x \sum_i \sum_{\sigma=-S}^{+S} (X_i^{s,\sigma} + X_i^{\sigma,s}) + \frac{1}{2}J_z N S^2 m^2 + \frac{1}{2}V_q z N \langle q \rangle^2. \end{aligned} \quad (5)$$

Here,  $B = zJSm$  is the Weiss field, where  $z = 6$  is the number of the nearest neighbors and  $m = \frac{\langle \hat{S}^z \rangle}{S}$  is the magnetization, and  $N$  is the number of sites of the crystal lattice. We consider the two-sublattice antiferromagnet, where the magnetization of the sublattice is  $m$ .

The set of the eigenfunctions of the Hamiltonian (5) can be represented in the form

$$|\varphi_k\rangle = \sum_{n_{\text{ph}}=0}^{N_{\text{ph}}} \left[ a_{n_{\text{ph},k}} |2, 0, n_{\text{ph}}\rangle + \sum_{s_z=-S}^{+S} b_{n_{\text{ph},s_z,k}} |1, s_z, n_{\text{ph}}\rangle \right], \quad (6)$$

Here,  $|\alpha, s_z, n_{\text{ph}}\rangle = |\alpha, s_z\rangle |n_{\text{ph}}\rangle$  is the orthonormalized basis of functions in the form of the direct product of the eigenstates of spin projection operators  $|\alpha, s_z\rangle$ ,  $s_z = -S, (-S+1), \dots, +S$  in the case of the HS state ( $\alpha = 1$ ) and  $s_z = 0$  for the LS state ( $\alpha = 2$ ) and the harmonic oscillator  $|n_{\text{ph}}\rangle = \frac{1}{\sqrt{n_{\text{ph}}!}} (a^\dagger)^{n_{\text{ph}}} |0, 0, \dots, 0\rangle$ ,  $n_{\text{ph}} = 0,$

$1, 2, \dots, N_{\text{ph}}$ , where  $N_{\text{ph}}$  is the number of phonons beginning with which the energy of the ground state  $|\varphi_0\rangle$  is almost the same for  $n_{\text{ph}} > N_{\text{ph}}$ , i.e.,  $E_0(N_{\text{ph}} + 1) \approx E_0(N_{\text{ph}})$  (the error of the calculation is

below 1%). When considering various temperature effects, it is necessary to control the constancy of the energies  $E_k$  of the lowest excited states  $|\varphi_k\rangle$ . In other words,  $N_{\text{ph}}$  is the number of phonons that should be taken into account at a given electron–vibration coupling in order to form a “phonon coat” of the ground and lowest excited states. In our calculations,  $N_{\text{ph}} = 300\text{--}500$  depending on the used parameters and temperature. Multiphonon contributions to function (6) give Frank–Condon resonances at the excitation of such states [20]. Then, the quantum statistical averages of the magnetization  $\hat{m} = \hat{S}^z/S$ , displacement  $\hat{q}$ , and population of the HS state  $\hat{n}_{\text{HS}}$  have the form

$$n = \langle \hat{n}_{\text{HS}} \rangle = \sum_k p_k \left\langle \varphi_k \left| \sum_{\sigma} X^{\sigma, \sigma} \right| \varphi_k \right\rangle \quad (7)$$

$$= \sum_k \sum_{n_{\text{ph}}=0}^{N_{\text{ph}}} \sum_{s_z=-S}^{+S} p_k |b_{n_{\text{ph}}, s_z, k}|^2,$$

$$q = \langle \hat{q} \rangle = \sqrt{\frac{\hbar}{2M\omega}} \sum_k \sum_{n_{\text{ph}}=0}^{N_{\text{ph}}} p_k$$

$$\times \left\{ \begin{array}{l} \sqrt{n_{\text{ph}}} \left( a_{n_{\text{ph}}, k} a_{n_{\text{ph}}-1, k} \right. \\ \left. + \sum_{s_z=-S}^{+S} b_{n_{\text{ph}}, s_z, k} b_{n_{\text{ph}}-1, s_z, k} \right) \\ + \sqrt{n_{\text{ph}}+1} \left( a_{n_{\text{ph}}, k} a_{n_{\text{ph}}+1, k} \right. \\ \left. + \sum_{s_z=-S}^{+S} b_{n_{\text{ph}}, s_z, k} b_{n_{\text{ph}}+1, s_z, k} \right) \end{array} \right\}, \quad (8)$$

$$m = \langle \hat{m} \rangle = \sum_k p_k \langle \varphi_k | \hat{m} | \varphi_k \rangle \quad (9)$$

$$= \frac{1}{S} \sum_k \sum_{n_{\text{ph}}=0}^{N_{\text{ph}}} \sum_{s_z=-S}^{+S} p_k s_z |b_{n_{\text{ph}}, s_z, k}|^2.$$

Here,  $p_k = \exp\left(-\frac{E_k}{k_B T}\right) Z^{-1}$ , where  $Z = \sum_k \exp\left(-\frac{E_k}{k_B T}\right)$  is the partition function.

The metal–ligand bond length can be represented in the form  $l = l_0 + q$ , where  $l_0$  is the regular component caused by the anharmonicity of vibrations of the lattice and the anomalous contribution  $q$  caused by the vibronic interaction. In the absence of spin–orbit coupling, the equilibrium positions of ligands corresponding to minima of the potential energy in the LS and HS states are given by the expressions  $q_{\text{LS}}^0 = -\frac{g_1}{k_{\text{LS}}}$  and  $q_{\text{HS}}^0 = \frac{g_1}{k_{\text{HS}}}$ . For the chosen parameters presented

below,  $q_{\text{LS}}^0 = -0.09 \text{ \AA}$ ,  $q_{\text{HS}}^0 = 0.13 \text{ \AA}$ , and  $\Delta q^0 = q_{\text{HS}}^0 - q_{\text{LS}}^0 = 0.22 \text{ \AA}$ . Since the bond length  $l_0$  at  $T = 0$  is about  $2 \text{ \AA}$ ,  $\Delta q^0$  is about 10% of this value in agreement with the known difference between the ionic radii in the LS and HS states. It is seen that  $q_{\text{LS(HS)}}^0 = 0$  in the absence of the electron–vibration coupling and temperature-induced change in the volume of the system is possible only because of anharmonicity.

3. We consider the relaxation of the spin crossover complex placed in an equilibrium medium (thermostat) at a sudden light-induced excitation of the HS state to the LS state. The Hamiltonian of the total system can be written in the form

$$\hat{H} = \hat{H}_0 + \hat{H}_R + \hat{V}. \quad (10)$$

Here,  $\hat{H}_0 = \sum_k E_k |\varphi_k\rangle\langle\varphi_k|$  is the Hamiltonian of the cell (5);  $\hat{H}_R = \sum_q \hbar\omega_q b_q^\dagger b_q$  is the Hamiltonian of the thermostat, where  $b_q^\dagger (b_q)$  are the creation (annihilation) operators of phonons with the wave vector  $q$  in the thermostat; and  $\hat{V} = \hat{V}_{v\text{-ph}} + \hat{V}_{s\text{-ph}} \times \sum_q (g_{v\text{-ph}, q} b_q^\dagger a + g_{v\text{-ph}, q}^* b_q a^\dagger) + \sum_q (g_{s\text{-ph}, q} b_q^\dagger \hat{S}^+ + g_{s\text{-ph}, q}^* b_q \hat{S}^-)$  is the interaction operator between the spin crossover complex and thermostat, where  $a^\dagger (a)$  are the creation (annihilation) operators of quanta of local vibrations (vibrons) introduced above and  $g_{v\text{-ph}}$  and  $g_{s\text{-ph}}$  are the vibron–phonon and spin–phonon coupling constants, respectively.

We consider the dynamics of the system in terms of the reduced density matrix  $\hat{\rho}_0(t)$  using the generalized master equation [21]

$$\frac{\partial}{\partial t} \rho_{kl}^0 = -i\omega_{kl} \rho_{kl}^0 + \delta_{kl} \sum_{n \neq l} \rho_{nn}^0 W_{ln} - \gamma_{kl} \rho_{kl}^0. \quad (11)$$

Here,  $W_{ln} = \Gamma_{nln}^+ + \Gamma_{nln}^-$  and  $\gamma_{kl} = \sum_n (\Gamma_{knn}^+ + \Gamma_{lnl}^- - \Gamma_{llk}^+ - \Gamma_{llk}^-)$ , where

$$\Gamma_{mkl}^+ = \frac{1}{\hbar^2} \int_0^\infty dt \exp(-it\omega_{ln}) \text{Tr}_R (V_{mk}(t) V_{ln}(0) \rho_R(0)), \quad (12)$$

$$\Gamma_{mkl}^- = \frac{1}{\hbar^2} \int_0^\infty dt \exp(-it\omega_{mk}) \text{Tr}_R (V_{mk}(0) V_{ln}(t) \rho_R(0)). \quad (13)$$

Here,  $V_{mk}(t)$  are the matrix elements in the interaction representation and  $\omega_{kl} = \frac{E_k - E_l}{\hbar}$ . If  $\hat{Q}_0$  is the operator acting on the variables of only the subsystem of interest (in our case,  $\hat{Q}_0$  are the operators  $\hat{m}$ ,  $\hat{n}$ , and  $\hat{q}$ ), then

the average value of a certain observable defined by this operator is written in the form  $\langle \hat{Q}_0 \rangle = \text{Tr} \hat{Q}_0 \hat{\rho}^0(t)$ .

The standard calculations of the coefficients  $\Gamma$  appearing in Eq. (11) give

$$\Gamma_{nln}^+ = \Gamma_{nln}^{(v-ph)+} + \Gamma_{nln}^{(s-ph)+}, \quad (14)$$

$$\Gamma_{nln}^{(v-ph)+} \approx \gamma_0^{v-ph} [a_{nl}^2 n_{\text{BE}}(\omega_{ln}) + a_{ln}^2 (n_{\text{BE}}(\omega_{nl}) + 1)], \quad (15)$$

$$\Gamma_{nln}^{(s-ph)+} \approx \gamma_0^{s-ph} [s_{nl}^2 n_{\text{BE}}(\omega_{ln}) + s_{ln}^2 (n_{\text{BE}}(\omega_{nl}) + 1)], \quad (16)$$

where  $a_{ij} = \langle \varphi_i | a | \varphi_j \rangle$ ,  $s_{ij} = \langle \varphi_i | \hat{S}^+ | \varphi_j \rangle$ , and  $n_{\text{BE}}(\omega)$  is the Bose–Einstein distribution function. In our case,  $\Gamma_{nln}^+ = \Gamma_{nln}^-$  and  $\Gamma_{llk}^+ = \Gamma_{llk}^- = 0$ . The coefficients  $\gamma_0^{v-ph}$  and  $\gamma_0^{s-ph}$  in Eqs. (15) and (16) are determined by the constants  $g_{v-ph}$  and  $g_{s-ph}$ , respectively. As typical values of these coefficients, we used  $\tau_0^{v-ph} \sim \frac{1}{\gamma_0^{v-ph}} \sim 1$  ps and  $\tau_0^{s-ph} \sim \frac{1}{\gamma_0^{s-ph}} \sim 1$  ps corresponding to the experiments reported in [22, 23].

Figure 1 shows the calculated relaxation dynamics of (red line) the magnetization  $m$ , (blue line) the population of the HS state  $n$ , and (black line) the displacement  $q$  for the spin–orbit coupling parameters  $J_x =$  (upper panels) 0.01 and (lower panels) 0.05 eV. The calculations were performed taking into account the triple orbital degeneracy of the HS state at  $T = 100$  K with the parameters  $J = 28$  K (for  $\text{Fe}_x\text{Mg}_{1-x}\text{O}$ ) [24] and  $k = 7.5$  eV/Å<sup>2</sup>,  $\omega = 0.05$  eV,  $g_1 = 0.8$  eV/Å<sup>2</sup>,  $g_2 = 0.75$  eV/Å<sup>2</sup>, and  $V_q = 0.2$  eV/Å [25]. The time in the left and middle panels is given in units of  $\tau_0 = 10^{-12}$  s. The right panels show the Fourier spectral analyses of the magnetization  $m$ , the population of the HS state  $n$ , and (black line) the displacement  $q$  for the determination of the intensity and frequency of the spectral components of the solutions of Eq. (11). As the initial photoexcited state  $|\psi_0\rangle$ , we specified the state obtained from the ground state  $|\varphi_0\rangle = \sum_{n_{\text{ph}}=0}^{N_{\text{ph}}} [a_{n_{\text{ph},0}} |2, 0, n_{\text{ph}}\rangle + \sum_{s_z=-S}^{+S} b_{n_{\text{ph},s_z},0} |s_z, n_{\text{ph}}\rangle]$  by switching the quantum numbers  $\alpha$  and  $s_z$ . In particular, if the magnetic HS state is the ground state, the excited state  $|\psi_0\rangle = \sum_{n_{\text{ph}}=0}^{N_{\text{ph}}} [a_{n_{\text{ph},0}} |2, 0, n_{\text{ph}}\rangle + \sum_{s_z=-S}^{+S} b_{n_{\text{ph},s_z},0} |2, 0, n_{\text{ph}}\rangle]$  is low-spin and the elastic (phonon) system remains unchanged, i.e., holds in the initial state corresponding to the HS electron configuration of the  $d$  ion. In other words, such switching of the states implements the dynamic crossover of the cation, leaving unchanged the state of ligands. This switching is justified because the photoexcitation of the system from the ground, e.g., LS  $^1A_{1g}$  state in the experiment occurs

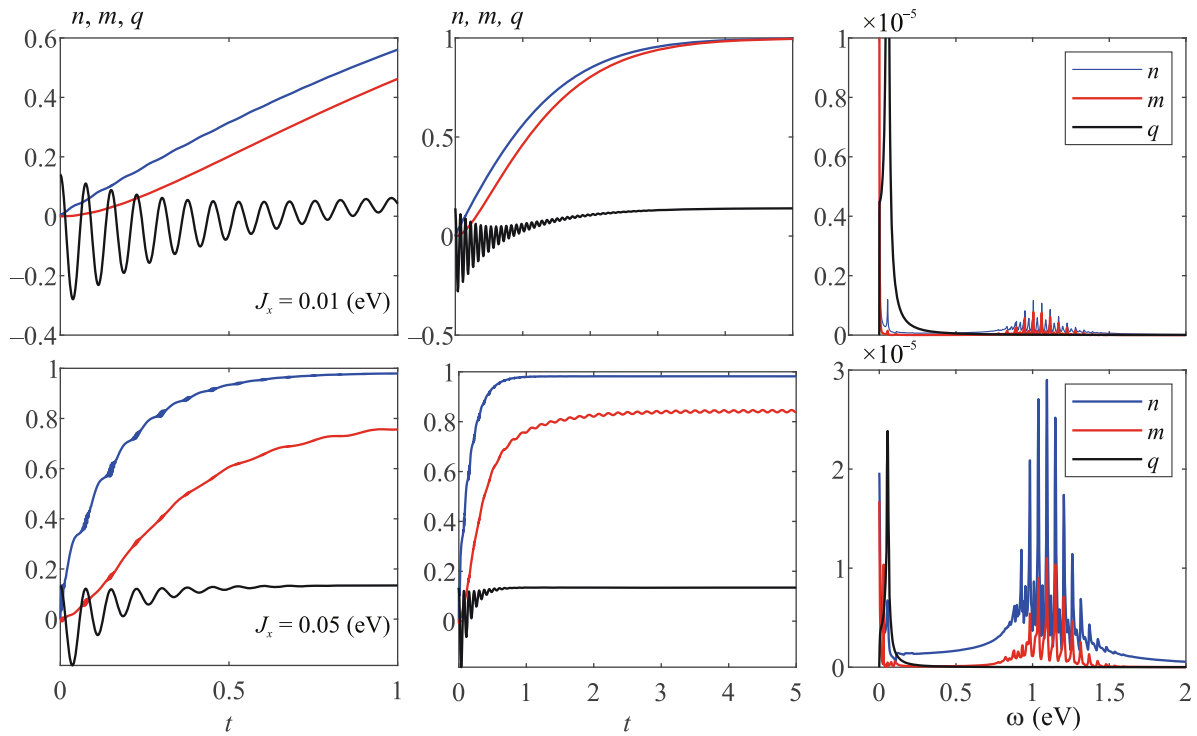
first to a certain intermediate  $^1T_{2g}$ ,  $^1T_{1g}$ , or charge-transfer state from which the system can rapidly return back to the ground state or transit through a cascade to the excited vibron HS state and, then, relaxes much more slowly to the ground state because of the phonon damping. In the case of the HS  $^5T_{2g}$  ground state, the intermediate state is the  $^5E_g$  term, from which the system transfers quite rapidly through a cascade to the excited vibron LS state and, then, relaxes much more slowly to the HS ground state because of the phonon damping [22, 23]. The characteristic time of cascade transition is less than 100 fs, whereas relaxation through a phonon ladder occurs in about 3 ps [22, 23]. For this reason, we do not consider primary cascade processes in the system and take the nonmagnetic vibron LS state as the initial state at  $t = 0$  in Eq. (11). The photoexcited state can be expanded in the basis of the eigenstates of the Hamiltonian of the isolated subsystem  $|\psi_0\rangle = \sum_k C_{0k} |\varphi_k\rangle$ , where  $C_{0k} = \langle \varphi_k | \psi_0 \rangle$ ; consequently, the initial density matrix has the form  $\hat{\rho}_{kk}^0(0) = C_{0k} C_{0k}^*$ .

At finite temperatures, the subsystem is in the state  $|\varphi_k\rangle$  with the probability  $p_k$ ; therefore, the initial density operator has the form  $\hat{\rho}^0(0) = \sum_k p_k |\psi_k\rangle \langle \psi_k| = \sum_k \sum_{ii'} p_k C_{ik} C_{i'k}^* |\varphi_i\rangle \langle \varphi_{i'}|$ , where  $|\psi_k\rangle = \sum_i C_{ki} |\varphi_i\rangle$ ,  $C_{ki} = \langle \varphi_i | \psi_k \rangle$ .

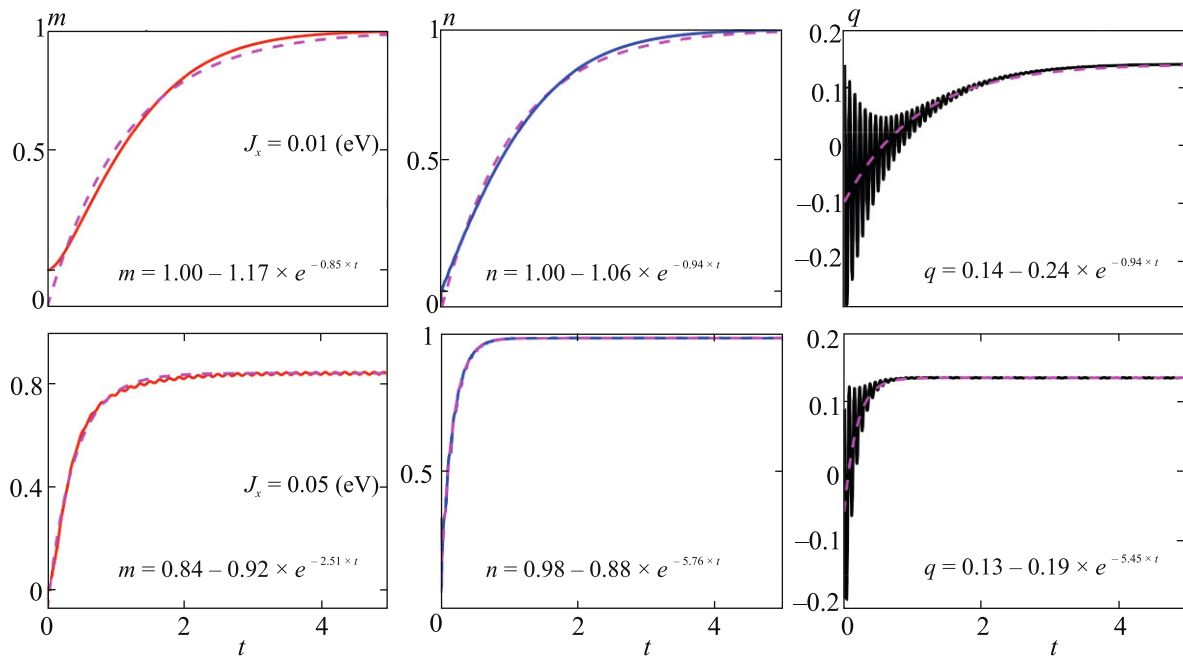
To determine the characteristic time of relaxation of photoexcited states, we used the exponential approximation  $y_i = y_{0i} + \eta_i e^{-\xi_i t}$  of the time dependences of the magnetization ( $i = m$ ), the population of the HS state ( $i = n$ ), and the displacement ( $i = q$ ), where  $\eta_i$  and  $\xi_i$  are the fitting parameters and the equilibrium values  $y_{0i}$  were found from the static self-consistent solution of the mean-field equations (7)–(9). Figure 2 shows these approximations for the spin–orbit coupling parameters  $J_x =$  (upper panels) 0.01 and (lower panels) 0.05 eV.

As seen in Figs. 1 and 2, the relaxation times for  $n$  and  $q$  are almost the same,  $\tau_n \approx \tau_q$ . This is not surprising because change in the bond length  $q$  is proportional to the ionic radius of the cation. The relaxation times are summarized in Table 1.

According to Figs. 1 and 2, it is possible to separate several time scales of the complex dynamics of the system: the period of oscillations of the magnetization  $m$ , the population of the HS state  $n$ , and the displacement  $q$  and the characteristic time of relaxation of the system to the ground state. Moreover, the time dynamics of the system are significantly different in the cases of weak and strong spin–orbit coupling. In particular, the dependences  $m(t)$  and  $n(t)$  at the spin–orbit coupling parameter  $J_x = 0.05$  eV exhibit a number of per-



**Fig. 1.** (Color online) Quantum relaxation dynamics of initially low-spin photoexcited Franck–Condon states at  $T = 100$  K for the spin–orbit coupling parameters  $J_x =$  (upper panels) 0.01 and (lower panels) 0.05 eV. The time in the left and middle panels is given in units of  $\tau_0 = 10^{-12}$  s. The right panels show the Fourier spectral analyses of (red line) the magnetization  $m$ , (blue line) the population of the HS state  $n$ , and (black line) the displacement  $q$ .



**Fig. 2.** (Color online) Exponential approximation  $y = y_0 + \eta e^{-\xi t}$  of the time dependences of the magnetization  $m$ , (blue line) the population of the HS state  $n$ , and (black line) the displacement  $q$  for the spin–orbit coupling parameters  $J_x =$  (upper panels) 0.01 and (lower panels) 0.05 eV.

**Table 1.** Characteristic relaxation times of the magnetization ( $\tau_m$ ), population of the HS state ( $\tau_n$ ), and metal–ligand bond length ( $\tau_q$ ) for two values of the spin–orbit coupling  $J_x$

$J_x$ (meV)	$\tau_m$ (ps)	$\tau_n$ (ps)	$\tau_q$ (ps)
10	1.18	1.06	1.06
50	0.40	0.18	0.18

turbations with intervals between them (wave packet or train of high-frequency waves with a vibrational energy of  $\sim 1$  eV). Narrow peaks in the Fourier spectrum of this train of high-frequency waves in the lower right panel of Fig. 1 are separated by a frequency interval of  $\Delta\omega = 58$  meV, which almost coincides with the lattice vibration energy  $\omega_{\text{LS}} = 55$  meV. This allows treating the train of high-frequency waves as Franck–Condon resonances correlating with the minima and maxima of oscillations of  $q(t)$ . These perturbations relax in a time of  $\sim \tau_q$ ; after that, the magnetization undergoes long-lived periodic oscillations with a period of 140 fs and an energy of 35 meV. The same frequencies are also revealed in the Fourier analysis for  $J_x = 0.01$  eV (Fig. 1, the upper right panel), but the amplitudes of oscillations are much smaller than those for the case  $J_x = 0.05$  eV (Fig. 1, the lower right panel). Such low-frequency oscillations of the magnetization were detected experimentally in FeBO<sub>3</sub> canted antiferromagnet subjected to a femtosecond pumping [26, 27]. In [26, 27], the initial HS ( $S = 5/2$ ) state of the Fe<sup>3+</sup> ion was excited to the intermediate spin state of the Fe<sup>3+</sup> ion with the spin  $S = 3/2$ , and in about 4 ps after the excitation, oscillations of the magnetization with a period of about 2 ps were observed. In our calculations, oscillations of the magnetization were established after the return of the electron and elastic systems to the equilibrium HS values in a time of about 2 ps and had a period of 0.14 ps. Since we do not consider in this work a model that corresponds to the scheme of the levels of the Fe<sup>3+</sup> ion and is adequate to FeBO<sub>3</sub>, it is impossible to expect quantitative coincidence with the experimental data. At the same time, the qualitative picture of long-lived magnetic oscillations revealed in our work is consistent with the data [26, 27].

4. To conclude, we have revealed for the first time oscillations of the magnetization and a complex multiscale time dynamics of relaxation of the magnetization, population of the HS state, and the cation–anion bond length in strongly correlated systems with spin crossover and long-range magnetic order. We hope that this work will stimulate further experimental studies of the ultrafast time dynamics of magnetically ordered systems with spin crossover.

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