Light-induced ultrafast dynamics of spin crossovers in LaCoO$_3$

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Ultrafast quantum dynamics relaxation of a photoexcited state in a strongly correlated spin crossover system LaCoO$_3$ under a sudden perturbation is considered with the density matrix generalized master equation. The magnetization and cobalt-oxygen bond length oscillations were found. The evolution of the electronic band structure during relaxation is calculated in the framework of the LDA+GTB method.

In LnCoO$_3$ the ground state of the Co$^{3+}$ ion is known to be in the low spin (LS) $^1A_{1g}$ state with $S = 0$, so the ground state is non magnetic. It is known also that the lowest excited high spin (HS) $^5T_{2g}$ term is separated from the LS one with rather small excitation energy (a spin gap), which is minimal for La (about 10 meV) and increasing for more heavy Ln ions [1]. That is why for LaCoO$_3$ spin state transition is known for a long time with heating [2–4]. This transition results from the thermal population of the HS- terms. Recently a new direction in the spin crossover study appears due to new experimental possibilities to switch a LS- state into the HS one by femtosecond irradiation and then to study the spin crossover dynamics by the X-ray spectroscopy methods with time resolution. Using X-ray free electron laser [5, 6] such dynamics has been studied in metal-organic complexes Fe(phen)$_2$(NCS)$_2$. For LaCoO$_3$ a first time-dependent LS-HS dynamics has been discussed theoretically in the paper [7] and studied with femtosecond soft X-ray spectroscopy in the paper [8] where an ultrafast metallization has been detected.

It is known that the ionic radii of the HS- and LS-states have quite large (about 10%) difference. It means that excitation from LS- to HS- state results in a remarkable local distortion. Therefore, a multiplicity fluctuation results in a strong electron-phonon anharmonicity. Previously we have studied dynamics in a model with HS/LS ionic states under high pressure that may induce spin crossover [9]. Femtosecond switching from HS to LS was considered in a sudden approximation, and the relaxation of the HS concentration, metal – ligand bond length and the local magnetization was obtained by a numerical solution of the generalized Master equations. Taking in mind possible ultrafast dynamics experiment we report here the results of the theoretical dynamics of LaCoO$_3$, where LS initial state is excited by a femtosecond pump. With heating LaCoO$_3$ undergoes a smooth insulator – metal transition, when concentration of the HS- state is above some critical value $n_{HS} = 0.85$, the semiconductor gap is closing [10]. Here we will discuss the LS/HS excitation dynamics, keeping in mind two features of LaCoO$_3$ that can be measured by the X-ray spectroscopy methods with time resolution. That is the time dependence of the Co-O bond length, and time dependent metallization.

Using the generalized master equation for the density matrix, we consider the ultrafast quantum relaxation dynamics of a photoexcited state in systems with a spin crossover under a sudden perturbation. The calculations are carried out taking into account the Coulomb and spin-orbit interactions in the framework of the Tanabe-Sugano theory (full multiplet theory) and the electronic-
vibrational interaction beyond the adiabatic approximation.

The Fig. 1 shows photoexcitation from the ground \(^1\)A\(_{1g}\) state to the \(^1\)T\(_{1g}\) state and relaxation process for the \(d^6\) electronic configuration of a transition metal ion in an octahedral ligands field. Various channels of relaxation and the appearance of relatively long-lived metastable states are possible.

When the system passes from the light-excited Frank-Condon state to the ground state, the temporal dynamics of the lattice, magnetic and electronic band structure is calculated. At each time step, a self-consistent calculation of the magnetization and occupation numbers of multielectron terms is performed. The electronic band structure is calculated using the LDA+GTB method [11], where the key role is played by the occupation numbers of multielectron states. For example, for \(d^6\)- ions, the population of the HS- state of more than 85% leads to a semimetallic type of band structure, while the ground unexcited LS- state is a nonmagnetic dielectric. The relaxation of the system is usually accompanied by magnetization oscillations and a change in the type of magnetic ordering (photoinduced magnetic transition), since the sign and magnitude of the interatomic exchange interaction (photoexcited Franck-Condon transition), because the term occupancy \(n_{HS}\) (the red dashed line marks the occupancy of 85%), and the bottom row shows the average value of the normal coordinate operator corresponding to the breathing vibrational mode of ligand’s \(q\) [Å].

Figure 3 presents the calculation results of the electronic band structure before (a) photoexcitation, in the LS- state, and after (b) at times \(t_1\) and \(t_2\) (Fig. 2), corresponding to an occupancy of the HS- state of 85%. In the time interval \(t_1 \leq t \leq t_2\), a semimetallic state (b) is realized, in contrast to the dielectric ground state (a).

To conclude, we have revealed magnetization temporal oscillations and a complex multiscale time dynamics relaxation of the magnetization, HS-state population, and the cation-anion bond length in strongly correlated LaCoO\(_3\) systems. In the process of relaxation, a dielectric – semimetal – dielectric transition was discovered. We hope that this work will stimulate further experimental studies of the ultrafast time dynamics of magnetically ordered and non-ordered systems with spin crossover.

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FIG. 2. Quantum relaxation dynamics of the Frank-Condon $^1T_{1g}$ state, photoexcited from the ground LS- state. The upper row shows the magnetization $m = \langle \hat{S}^z \rangle$ for the sublattice, the middle row shows the term occupancy $n_{HS}$, and the bottom row shows the average value of the normal coordinate operator corresponding to the breathing vibrational mode of ligand’s $q$ [Å]. The red dashed line marks the term occupancy of 85%. Everywhere, the time along the abscissa is given in units of $t_0 = 10^{-12}$ sec. Calculations were performed for the following parameter values: Racah parameters $B = 1065$ cm$^{-1}$ (0.132 eV), $C = \gamma B$, $\gamma = 4.808$; spin-orbit coupling constant $\xi = 400$ cm$^{-1}$ (0.0496 eV); electron-vibration coupling constants linear $g_1 = 2.2$ eV/Å and quadratic $g_2 = 0.5$ eV/Å$^2$ in the lattice displacement; interatomic exchange interaction $J_{HS-HS} = 2.43$ meV (AFM), $J_{IS-IS} = 1.38$ meV (FM), $J_{HS-IS} = 0.6$ meV (AFM).

FIG. 3. Effect of HS optical population on LaCoO$_3$ quasiparticle spectrum. (a) in the LS- state before optical excitation, the band structure is of the insulator type; (b) quasiparticle spectrum at $t_1 = 817 t_0$ and at $t_2 = 1.71 \times 10^5 t_0$ (Fig. 2), the band structure is of the semimetal type at $t_1 < t < t_2$ with electrons and holes at the chemical potential. The red dashed line shows the chemical potential. $G(0,0,0)$, $M(\pi,\pi,0)$, $X(\pi,0,0)/(0,\pi,0)$, $R(\pi,\pi,\pi)$ are symmetric points of the Brillouin zone. More/less dark color of the dispersion curves corresponds to the more/less quasiparticle spectral intensity. Calculations were performed using the GTB method for the following parameter values: Racah parameters $B = 1065$ cm$^{-1}$ (0.132 eV), $C = \gamma B$, $\gamma = 4.808$; hopping parameters $t_{pd}^s = 1.57$ eV, $t_{pd}^p = 0.84$ eV, $t_{pp} = 0.3$ eV; charge transfer energy $\Delta_{CT} = \varepsilon_d - \varepsilon_p = 2.4$ eV [10].