Model of ultrafast demagnetization driven by spin-orbit coupling in a photoexcited antiferromagnetic insulator Cr$_2$O$_3$

Feng Guo, Na Zhang, Wei Jin, Jun Chang

College of Physics and Information Technology, Shaanxi Normal University, Xi'an 710119, China

We theoretically study the dynamic time evolution following laser pulse pumping in an antiferromagnetic insulator Cr$_2$O$_3$. From the photoexcited high-spin quartet states to the long-lived low-spin doublet states, the ultrafast demagnetization processes are investigated by solving the dissipative Schrödinger equation. We find that the demagnetization times are of the order of hundreds of femtoseconds, in good agreement with recent experiments. The switching times could be strongly reduced by properly tuning the energy gaps between the multiplet energy levels of Cr$^{3+}$. Furthermore, the relaxation times also depend on the hybridization of atomic orbitals in the first photoexcited state. Our results suggest that the selective manipulation of electronic structure by engineering stress-strain or chemical substitution allows effective control of the magnetic state switching in photoexcited insulating transition-metal oxides.

PACS numbers: 75.78.Jp, 82.50.–m, 82.53.-k, 63.20.kd

INTRODUCTION

In recent years, growing attention has been drawn to the photodriven ultrafast control of the quantum states and the physical properties in solid-state and molecular systems. In addition to the great theoretical interest in understanding the nonequilibrium dynamics in materials, it could be applied technically to the magnetic or electronic recording. The photoinduced change of physical properties is often attributed to thermal effects because the photon energy eventually is redistributed among interacting charge, spin, and lattice degrees of freedom, and increases the system temperature instantly. On the other hand, photoirradiation may induce non-thermal metastable states or transient phases with optical, magnetic and electric properties distinct from that of the ground states.

Among these light-responsive materials, the ferromagnetic materials have been brought into sharp focus by laser-induced demagnetization since Bigot and coworkers found the ultrafast dropping of magnetization in nickel film following optical pulses in 1996. Until recently, the ultrashort pulses of light are applied to manipulate the ultrafast processes in the antiferromagnets. Indeed, antiferromagnetic (AFM) materials have more advantages than ferromagnets. For example, they are insensitive to external magnetic fields stable in miniaturization and much faster in controlling spin dynamics.

AFM insulator Chromium oxide (Cr$_2$O$_3$) has been the subject of study since the 1960s and its electronic and static optical properties are now well understood. However, the ultrafast dynamic demagnetization processes were not probed until recently. The time-resolved second harmonic generation is applied to probe the time evolution of the magnetic and structural state following laser illuminations in the AFM insulator. Variations in the pump photon-energy lead to either localized transitions within the metal-centered states of the Cr ion or charge transfer between Cr and O. Despite its relevance to industrial technology, the ultrafast processes of demagnetization are not well understood from quantum nonequilibrium dynamics. To selectively control the demagnetization rate is still at a tentative stage in experiments.

In this paper, we first construct a local quantum-mechanical demagnetization model of the photoinduced electron states in Cr$_2$O$_3$. The effects of the energy dissipations are taken into account by a dissipative Schrödinger equation. We simulate the time evolution of the excited states following 1.8 eV and 3.0 eV light illumination and find that the decay times from the high-spin quartet states to the low-spin doublet states range from 300 femtoseconds (fs) to 450 fs, in line with the experiments. We show that the ratio of the energy gap to the electron-phonon self-energy has a marked impact on the demagnetization times. The decay times are also influenced by the hybridization of atomic orbitals in the first photoexcited state.

DEMAGNETIZATION MODEL

A typical static energy-level scheme of a Cr$^{3+}$ metal ion is shown in Fig. 1. The metal ion is in close proximity to oxygen octahedral surrounding and the five-fold degenerate 3d orbitals are split into a lower threefold-degenerate $t_{2g}$ and an upper twofold-degenerate $e_g$ orbitals by the crystal field with O$_6$ symmetry. Due to the Hund coupling, the ground state, less than half filled, is a high-spin ($S = 3/2$) $^4$A$_2$ ($t_{2g}^3$) configuration. Early in 1963, McClure reported the polarized optical absorption spectrum of Cr$_2$O$_3$ with the wavelength ranging from 300 to 800 nm in thin single-crystal plates. Two broad absorption bands are observed in the range of 400–800 nm corresponding to the transitions of the 3d electron shell from the $^4$A$_2$ ground-state level to the excited-state levels, $^4T_1$ ($t_{2g}^2e_g^1$) and $^4T_2$ ($t_{2g}^2e_g^1$), respectively.
FIG. 1. On the left: schematic absorbance of chromium oxide based on the spectrum measurements found in Ref. Two broad absorption bands located in the range of 1.8-3.0 eV correspond to the spin-allowed transition from the $^4A_2$ ground state to the $^4T_2$ and $^4T_1$ quartet states. The three sharp lines are associated with the spin-forbidden transitions to the $^2T_2$, $^2E$ and $^2T_1$ doublet states. On the right: energy-level scheme of Cr$_2$O$_3$. $R$ represents the coordination along the metal-ligand coordinate. $\Delta$ and $\varepsilon$ are the energy gap between the lowest vibrational levels and the electron-phonon self-energy difference between two oscillation states, respectively. The central energy value $E_i$ of the absorption spectrum is indicated by a line segment. In some cases, $E_i$ is different from the energy value of the lowest vibrational level owing to different electron-phonon couplings, e.g. in the $^4T_2$ and $^4T_1$ states. Here, we have set the ground state energy to zero.

Therefore, we first map the spin-boson-like model to an alternative model, where the electronic levels are coupled to a single harmonic mode damped by an Ohmic bath. The memory effects could be effectively taken into account by the time evolution of the strength of the harmonic mode. Here, the correlations between electrons are taken into account by the renormalization of the electronic state energies. The local system Hamiltonian is written as

$$H_S = \sum_i E_i c_i^\dagger c_i + \hbar \omega a^\dagger a + \sum_i \lambda_i c_i^\dagger c_i (a^\dagger + a)$$

$$+ \sum_{ij} V_{ij} (c_i^\dagger c_j + c_j^\dagger c_i),$$

where $c_i^\dagger, c_i$ gives the occupation of the multiplet $i$, $V_{ij}$ is the coupling constant that causes a transition between energy level $j$ and $i$, $a^\dagger$ is the creation operator for the harmonic phonon with frequency $\omega$. We further define the electron-phonon self-energy difference $\varepsilon_{ij} = (\lambda_i - \lambda_j)/\hbar \omega$ and the energy gap $\Delta_{ij} = (E_i - \lambda_i^2)/\hbar \omega - (E_j - \lambda_j^2)/\hbar \omega$ between two states, where variations in the electron-phonon coupling strength $\lambda_i$ change the equilibrium positions of different states. (see Fig. 1).

We describe the time evolution of the local open quantum system with the dissipative Schrödinger equation

$$i\hbar \frac{d\psi(t)}{dt} = (H_0 + iD)\psi(t),$$

where $H_0$ is the the Fröhlich transformation of the Hamiltonian $H_S$, $D$ is a dissipative operator that describes the bath induced state transfer.

$$D = \frac{\hbar}{2} \sum_k \frac{d \ln P_k(t)}{dt} |\psi_k><\psi_k|.$$

Here, $P_k(t) = |c_k(t)|^2$ is the state probability and $|\psi(t) >= \sum_k c_k(t) |\psi_k >$. The time evolution of the probability of multiplet $i$ with $n$ excited phonon modes is given by

$$d P_{in}(t) \frac{dt}{dt} = -2n \Gamma P_{in}(t) + 2(n+1) \Gamma P_{i,(n+1)}(t),$$

with $\Gamma = \pi \rho \sqrt{\omega^2/\hbar}$, the environmental phonon relaxation constant. According to the Jablonski energy diagram, $1/(2\Gamma)$ ranges from 0.01 picosecond (ps) to 10 ps. In this paper, we set $1/(2\Gamma) = 0.1$ ps.

**DEMAGNETIZATION PROCESS**

Since the spin-flip is forbidden in photoexcitation, the first photoexcited states starting from the $^4A_2$ ground
state are $^4T_2$, $^4T_1$, and the metal-ligand charge transfer $^4MLCT$ ($t_{2g}^2L^1$) quartet states, depending on the energies of photoexcitation. Here, $L^1$ denotes that an electron transfers to ligands. After the light illumination, the system decays to a relatively long-lived metastable state, e.g., the $^2T_1$ and $^2E$ doublet states in Cr$_2$O$_3$. Importantly, a long lifetime of the excited energy level promises to be a candidate to develop a potential laser device. In order to understand the dynamic process, we first need to determine the energies of the states involved in the cascading process. According to the absorption spectra, the central energies $E_1$ of the $^2E$, $^2T_1$, $^4T_2$, $^2T_2$, $^4T_1$, and $^4MLCT$ states locate around 1.7, 1.76, 2.1, 2.45, 2.75, 3.3 eV, respectively. Next, we need to establish an appropriate range of interaction parameters. The strength of the interaction between the Cr ion and its surrounding oxygen anions can be obtained from ab initio calculations. The change in energy for different configurations is close to parabolic for an adiabatic change in the Cr-ligand distance. From the change in equilibrium distance or the optical absorption and luminescence spectra, we can obtain the Huang-Rhys factor $g \approx 4$ between the doublets (e.g. $^2E$, $^2T_1$ and $^2T_2$) and the quartet states (e.g. $^4T_2$ and $^4T_1$) [23] We assume the Huang-Rhys factor $g \approx 0$ between the ground state and $^4MLCT$ according to the sharp absorption line. Correspondingly, the difference of electron-phonon self-energy $\epsilon_{ij}$ is equal to $g\hbar\omega$ and the electron-phonon coupling constant $|\lambda_i - \lambda_j| = \sqrt{\epsilon_{ij}\hbar\omega}$. The spin changes during the transfer from a quartet to a doublet state, and the coupling $V$ between the two different spin states is generally accepted to be due to the SOC. We take the strength of SOC around 0.03 eV in Cr ions [34,35]. Strongly coupled to the optically excited electrons, the optical phonon modes could be observed by Raman spectroscopy. Owing to the symmetry of Cr$_2$O$_3$, there are seven Raman modes, two with $A_{1g}$ symmetry and five with $E_g$ symmetry, and the longer wavelengths corresponding to the $E_g$ modes [24]. We take the $E_g$ mode value $\hbar\omega = 0.075$ eV, which dominates the relaxation at the 1.8 eV pumping, and $A_{1g}$ mode $\hbar\omega = 0.065$ eV, the main damping phonon at 3.0 eV photon excitation [31].

The 1.8 eV photoexcitation results in the transition from the $^4A_2$ ground state to the $^4T_2$ excited state. An electron in the $t_{2g}$ orbital is locally excited to the $e_g$ orbital by the illumination. Such a transition yields an elongation of the Cr–O band length of several tenths of an Ångstrom since the change from a $t_{2g}$ to an $e_g$ charge distribution leads to a stronger repulsion between the Cr and the O ligands [29]. The bond length change leads to different electron-phonon couplings between the two states, thereby forming a Franck-Condon continuum [33]. Under the action of SOC and electron phonon interaction, the first excited state relaxes to the long lived states, namely, the $^2T_1$ and $^2E$ doublet states. The energy gap between $^2T_1$ and $^2E$ is small, e.g. around 0.06 eV, therefore the $^2T_1$ and $^2E$ populations are often combined for kinetic purposes [29]. In Fig. 2 we show the time evolution of the three states involved in the ultrafast demagnetization process by solving the dissipative Schrödinger equation. The starting state is $^4T_2$, excited from the ground state. The $E_g$ phonon mode with $\hbar\omega = 0.075$ eV dominates the relaxation [31]. Therefore, the self-energy difference $\epsilon$ between the metal-centered quartet and doublet is 0.3 eV, with the Huang-Rhys factor $g = 4$. The quartet state and the doublet state are mediated by SOC, i.e. $V = 0.03$ eV. The energy gap $\Delta$ between $^4T_2$ and $^2T_1$ is 0.04 eV, and 0.1 eV between $^4T_2$ and $^2E$. The 0.04 eV and 0.1 eV energy gaps are indicated in the obvious oscillations with the periods around 100 fs and 40 fs, respectively in the time evolution of both the quartet and doublet states. We find that the probability of the $^4T_2$ state falls quickly and the sum of the probability of the $^2T_1$ and $^2E$ states increases in the first 0.5 ps. Fitting the curves using kinetic rate equations, the rise time constant of the sum of the two doublet states are around 400 fs, which agrees well with the experiments by the time-resolved second harmonic generation [23].

The decay time of a photoexcited state strongly depends on the ratio of the energy gap to the electron-phonon self-energy difference, which has been demonstrated in transition-metal complexes [33]. When the ratio $\Delta/\epsilon$ ranges from 0.5 to 1.5, the fastest decay occurs. In engineering, the energy gap between the multiplets could be changed by distortion stress, strain or chemical substitution of ligands, which provides a feasible approach to adjust the demagnetization time. For example, since the gap between $^4T_2$ and $^2T_1$ is very small, $\Delta = 0.04$ eV, it may result in a longer decay time. We found that provided the gap increases 0.2 eV, close to $\epsilon = g\hbar\omega = 0.3$ eV, the demagnetization time is strongly reduced to around 100 fs, a quarter of the original period, as shown in Fig. 2. Comparing with Fig. 2, the probability oscillations are strongly suppressed by the faster energy dissipation.
The time evolution of the state probabilities with different energy gaps between $^4T_2$ and $^2T_1$ at 1.8 eV photon pumping. (a) The gap $\Delta$ between $^4T_2$ and $^2T_1$ is 0.24 eV, close to the corresponding $\varepsilon=0.3$ eV, the demagnetization time reduces to 100 fs; (b) $\Delta = 0.34$ eV, the relaxation time is around 150 fs. The dashed line (blue) and the solid line (green) give the probabilities of finding $^4T_2$ and the sum of $^2T_1$ and $^2E$, respectively.

On the other hand, if we only vary the photoexcitation energies from 1.8 eV to 2.1 eV and keep all the other parameters the same, the time evolutions of the three states change slightly from Fig. 2 (not shown).

The 3.0 eV photon energy is supposed to excite the $^4A_2$ ground state to the $^4T_1$ metal-centered state and/or the $^4MLCT$ metal-ligand charge transfer state. Due to the electron-phonon interaction, SOC and orbital hybridization, the first excited state finally reaches the $^2T_1$ and $^2E$ doublet states via the transit $^4T_1, ^2T_2$ and $^4T_3$ states. In pure octahedral symmetry, there is no coupling between $^4MLCT$ and $^4T_{1,2}$, since the $e_g$ orbital states do not couple to the ligand $\pi^*$ states. Nevertheless, since the nonequilibrium charge transfer often leads to a lower structural symmetry, a small hybridization between the two quartet states should be presented, depending on the amount of distortion. The weak hopping energy between the ligands $\pi^*$ or $\pi$ and the metal ion’s $e_g$ orbitals is of the order of hundredths eV. Our numerical calculations are not sensitive to the change in the hybridization from 0.03 eV to 0.09 eV. In Fig. 3 we set the hybridization parameter 0.05 eV between $\pi^*$ and $e_g$. The metal-centered quartet and doublet states are supposed to be mediated by SOC, $V=0.03$ eV. There is no direct coupling between $^4MLCT$ and the doublet states since no interaction allows spin-flip and charge transfer synchronously. The main damping phonon is the $A_{1g}$ phonon mode with $\hbar\omega = 0.065$ eV. Consequently, $\varepsilon$ between the metal-centered quartet and doublet states is 0.26 eV with the Huang-Rhys factor $g = 4$. First, we assume that the electrons in the ground state is excited to the $^4MLCT$ state. From the time evolution of the states, we find that the rise time constant of the doublets is around 300 fs by fitting the curves using kinetic rate equations. Next, it has been pointed out that the first excited state at high energy excitation could be the mix of $^4T_1$ and $^4MLCT$. Taking a mixed first excited state $a[^4MLCT] + \sqrt{1-a^2}[^4T_1]$, the fitting rise time values of the doublets are 450 fs with the mix constant $a^2 = 0.75$, 380 fs for $a^2 = 0.5$, and 300 fs for $a^2 = 0.25$, respectively. In Fig. 4 the time-dependent occupations of the states involved in the demagnetization process are shown, with the mix constant $a^2 = 0.25$. Interestingly, the $^2T_2$ state is often ignored in some literatures because its absorption is too narrow to be resolved in optical spectra. However, if the $^2T_2$ state is omitted in our model, we find that the probability of $^4T_1$ plateaus at value 0.1 from 3 ps after the pumping. An extension of the time evolution up to 0.1 ns confirms that the neglect of $^2T_2$ results in an incomplete decay of $^4T_1$, which is inconsistent with the experiments. Therefore, the time scale of ultrafast demagnetization depends not only on the pumping energy, but also on the electric configuration of energy levels, the spin-orbit and electron-phonon couplings.

CONCLUSION

To conclude, we have presented a quantum-mechanical demagnetization model for the locally photoinduced electron state in Cr$_2$O$_3$. Using the dissipative Schrödinger equation, the environmental energy dissipations are considered. We numerically simulated the time evolution of the excited states following 1.8 eV and 3.0 eV photon excitation. The decay times are consistent with experiments on the order of hundreds of femtosecond from the high-spin quartet states to the low-spin doublet states. Both the spin-orbit coupling and electron-phonon coupling take important roles in the ultrafast demagnetization processes. We have shown that the ratio of the energy gap to the electron-phonon self-energy has strong impact on the demagnetization times. The hybridization of the atomic orbitals in the first photoexcited state...
also affects the decay times. We further expect that the demagnetization times could be selectively controlled by the engineering stress-strain or chemical substitution of ligands in insulating transition-metal oxides.

ACKNOWLEDGMENTS

We are thankful to Jize Zhao, Hantao Lu and Ning Li for fruitful discussions. F. G. and J. C. are supported by the Fundamental Research Funds for the Central Universities, Grant No. GK201402011. W. J. is supported by NSFC 11504223.