All-Optical Subpicosecond Magnetic Switching in NiO(001)

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Combining optical control theory with *ab initio* quantum chemistry and electronic crystal field theory we explore the laser induced femtosecond spin dynamics. We propose a scenario for ultrafast all-optical magnetic switching that results from the combination of spin-orbit coupling with appropriately shaped short laser pulses. We find that the application of the theory to the multiplet states within the gap of NiO(001) predicts for the first time the possibility of all-optical spin switching within 100 fs. The switching can be observed using any of the multiplets as the intermediate state.

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The tremendous increase in storage density and read-write speed in magnetic storage media is reaching its physical limits. Actual read-write processes take place on the order of nanoseconds. Newly developed methods, such as precessional switching [1], have shown the potential to reach subnanosecond time scales, while competing nonmagnetic optical technologies have already demonstrated even faster switchings [2,3]. Therefore, the need for a speedup of magnetic dynamics is imminent. Recent pump-probe experiments have shown a fast decay of the magneto-optical signal occurring on the subpicosecond time scale in Ni using the time-resolved (TR) magneto-optical Kerr effect (MOKE) [4], TR second harmonic generation (SHG) [5] and two-photon photoemission (TPPE) [6], $CoPt_3$ using TR-MOKE [7], and Co using TPPE [8]. Recent experiments on Ni provided evidence for a state filling effect (bleaching) during the very first instants of the dynamics, followed by a true demagnetization after about 200 fs [9,10].

These results inspired us to investigate one possible option for the speedup of magnetic dynamics, namely, the use of ultrashort laser pulses together with the leveraging of spin-orbit coupling (SOC) for all-optical spin switching. Our main idea is to bypass the small energy magnetic transition (Zeeman splitting, gyromagnetic energies, or magnetic anisotropy barriers, 1–100 μeV) which automatically leads to nanosecond switching times, by two electric, laser induced, transitions via a higher excited state (on the order of 1 eV). In order to provide spin switching, this excited state has to be spin mixed. To achieve this spin-mixed state, a twofold degenerate level has to be split by SOC. Such a transition through a highly excited state can indeed take place in the femtosecond time regime [11]. To obtain this gain in speed and to arrive at the same final (switched) state $|0\rangle_{\downarrow}$, both transitions must be coherently controlled. In this work, based on electronic theory, we analyze the possibility of such an all-optical spin switching on NiO(001). The key results are (i) the electronic structure of NiO allows one to exploit the previously reported scenario [12] yielding magnetic switching within 150 fs (see Fig. 3), (ii) spin switching is obtained from *ab initio* theory for the first time, and (iii) it can be obtained using states of different symmetries as the intermediate state.

Coherent control of electron dynamics is a well developed field in semiconductor physics. In this work, we extend these ideas to the magnetic case. The electron dynamics is calculated using our own implementation of the first steps of the COMPUTE algorithm [13], which has been successfully used for NMR spectra. We exclusively employ this algorithm in the time domain, since we are mainly interested in the time evolution.

Previous theoretical works have successfully taken a first attempt to disentangle the magnetic dynamical processes taking place on the various time scales: (i) ''bleaching'' [blocking of the response to the probe pulse by state filling (1 fs)] [14], (ii) magnetic dephasing electron-spin relaxation (5–10 fs) [14], (iii) genuine demagnetization (20–40 fs) [15], and (iv) spin-lattice relaxation (304 ps for Ni) [14]. Note that processes (iii) and (iv) rely on spin-orbit coupling while (i) and (ii) do not. These theoretical results demonstrated a considerable amount of control of the magnetic dynamics by an appropriate choice of the laser pulse parameters (central pulse frequency, amplitude, and pulse duration) in metallic Ni but failed to obtain a controlled *switching* of the magnetic moment [16]. This is due to the fact that, in metals, the electrons are excited into dispersive bands, in which the coherence is lost very fast and control is impossible. Thus the use of systems with discrete levels, such as nanoparticles, or gap states in insulators may be preferable.

To generate a fast transition between two almost degenerate states with different spins we need a laser excitation to a highly excited state, which is a spin-mixed state due to SOC, and back to the state of opposite spin. The conservation of angular momentum requires one to compensate any change of spin by some kind of reservoir. In the absence of other interactions, it is the laser field that

acts as a reservoir of angular momentum. Since electric dipolar optical transitions are spin conserving, the inclusion of SOC is necessary for a transfer of angular momentum between spin and orbital degrees of freedom. The latter can be exchanged with the angular momentum of the laser beam, when the light is circularly polarized. With such considerations in mind, the minimum system required for obtaining all-optical spin switching is a four-level system as shown in Fig. 2 in Ref. [12]. The model clearly showed the feasibility of all-optical spin switching within a few femtoseconds.

Magnetic gap states are present in NiO, which is a charge transfer insulator, having a gap of 4.3 eV and magnetic moment of $1.9\mu_B$ per Ni atom [17]. Its multiplet states within the gap are accessible by *d-d* excitations and may offer a scenario for this controlled dynamics. Density-functional theory-based theories (local-density approximation + U, self-interaction correction, and Green's function methods) cannot give intraband multiplets. Thus, we employ *ab initio* quantum chemistry which can tackle these intragap multiplet states. In addition to the high-level treatment of electron-electron interaction, which captures various relaxation processes [18] on a quantum mechanical level, this method guarantees a rapid convergence towards the thermodynamic limit, as is demonstrated by the comparison of our quantum chemical cluster calculation with surface and bulk experimental data (Table I). The fact that NiO is an antiferromagnet adds the advantage that the switching of the magnetic moment should not require any net exchange of angular momentum with the laser but makes it more difficult to measure the changes in the state. This last problem can be solved by TR-SHG measurements, with the additional advantage of also addressing *d-d* transitions, which are hardly visible in linear optics. In the static case, recent SHG measurements by Fiebig *et al.* [21] on bulk NiO have already indicated resonant magnetic lines within the fundamental gap which can be used for the imaging of antiferromagnetic domains. However, neither the surface optical response [22] nor the spin dynamics have been experimentally investigated on these materials so far. First theoretical attempts describing TR-SHG on NiO(001) have been performed by Trzeciecki *et al.* [23]. To obtain the spin dynamics of this material we use the following Hamiltonian:

$$H(t) = H_0 + H_1(t), \tag{1}$$

$$H_0 = \sum_{\nu\sigma\vec{k}} \varepsilon(\vec{k}) \cdot n_{\nu\sigma}(\vec{k}) + \sum_{i,j,k,l,\sigma,\sigma',\sigma'',\sigma'''} U_{i\sigma,j\sigma',k\sigma'',l\sigma'''} c^{\dagger}_{i\sigma} c^{\dagger}_{j\sigma'} c_{l\sigma'''} c_{k\sigma''}, \tag{2}$$

$$H_1(t) = \xi \vec{s} \cdot \vec{l} + \vec{p} \cdot \vec{E}(t). \tag{3}$$

To obtain the electronic structure of NiO we solve the time-independent many-body Hamiltonian (H_0). The first term in H_0 corresponds to the single-particle contribution, while the second one describes the electron-electron correlation. Since the states of interest are strongly localized [gap states of the NiO(001) surface], the $\vec{k}$ dependence of the band structure can safely be disregarded. Because of the strong electronic correlation of NiO we use *ab initio* quantum chemistry [24] up to the level of quadratic configuration interaction approach with single and double virtual excitations followed by a fourth-order perturbative treatment of triple excitations [QCISD(T)] to obtain the low-lying states of a $(NiO_5)^{8-}$ and a $(NiO_6)^{10-}$ cluster which is subsequently embedded in a surface or bulk large surrounding [25]. These clusters reflect the local symmetries of the (001) surface of NiO and the bulk, respectively. The results obtained for the lowest *d-d* multiplet states are in good agreement with experiments [19,20], as can be seen in Table I.

In order to obtain the higher lying states of the intragap multiplets we use a ligand field theory, which exploits the symmetry of the system, fitted to the low lying states. This allows us to extend the results to the whole set of two-hole multiplet levels in NiO for the (001) surface (C_{4v} symmetry) as can be seen in the left column of Fig. 1.

For the spin dynamics we have to include $H_1(t)$. The first term in Eq. (3) is the spin-orbit coupling, taking into account only the spherical part. For the spin-orbit coupling parameter we have used the value $\xi = 0.1$ eV. The new level scheme obtained by the addition of this term is shown in the right column of Fig. 1. The time dependent part of H_1 corresponds to the interaction with the laser electric field, given by $\vec{E}(t) = \vec{E}_0 \exp(-i\omega_0 t)\sum_n \exp[-(\frac{t-t_0-n\mathcal{T}}{\tau})^2]$ [26]. For the electric dipole ($\vec{p}$) matrix elements, we used the values of Ref. [27].

We take a circularly polarized laser pulse in order to make it work also as an angular momentum reservoir. The main frequency of the laser is chosen to be in resonance with some excited levels, as shown in [11]. The duration of the pulse is adjusted to obtain the best possible switching. Several possibilities appear with the NiO levels; the first excited states are the (sixfold degenerate) ^{3}E in Fig. 1, which, in the presence of SOC, are split into five different

TABLE I. *d-d* transition energies for NiO bulk and (001) surface. Comparison between this work and experiment.

System	Transition	Excitation energy (eV) Experiment [19,20]	QCISD(T)
NiO	$^3A_{2g} \rightarrow {}^3T_{2g}$	1.05, 1.08, 1.10, 1.13	1.13
Bulk	$^3A_{2g} \rightarrow {}^3T_{1g}$	1.79, 1.86, 1.87, 1.95	2.10
	$^3B_1 \rightarrow {}^3E$	0.57, 0.60	0.53
NiO	$^3B_1 \rightarrow {}^3B_2$	1.00	1.17
Surface	$^3B_1 \rightarrow {}^3A_2$	1.30	1.21
	$^3B_1 \rightarrow {}^3E$	1.62	1.85

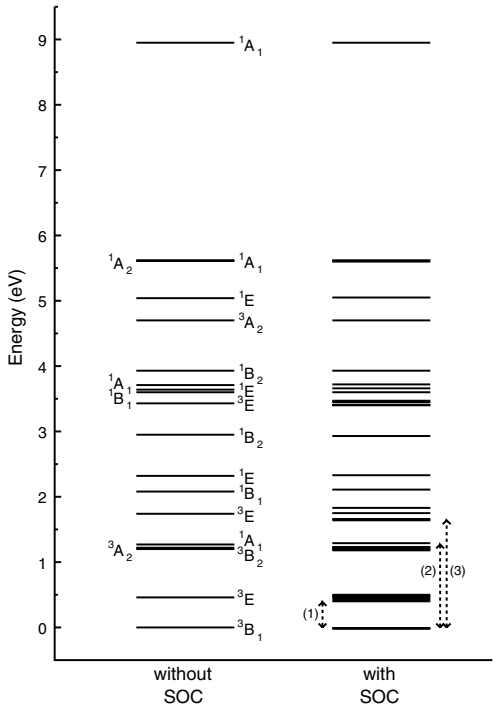

FIG. 1. Level scheme of the NiO(001) gap states obtained from the combination of *ab initio* quantum chemistry and ligand field theory.

states with energies between 0.40 and 0.50 eV. After trying with many frequencies around this interval, the best result is shown in Fig. 2, with a main frequency $\hbar\omega_0 = 0.422$ eV, as shown by the short vertical arrow labeled as (1) in Fig. 1 [28]. The result does not depend on the time delay between pulses. The oscillations observed in Fig. 2 are due to the interference between the different excited states that have been simultaneously populated and still retain some population after the pulse. The intensity needed in this case is much higher than in the four-level system. The reason is that in the four-level system, the efficiency of the laser to produce the excitation to the selected excited state is much higher, as well as the efficiency of SOC to mix the different spin states.

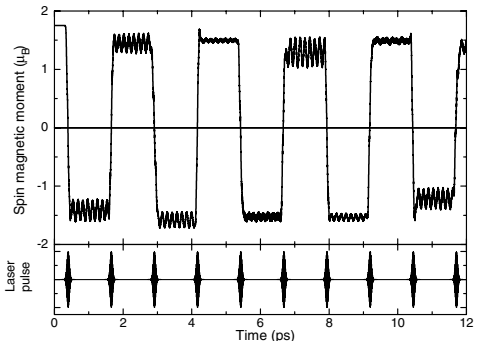

FIG. 2. Magnetic moment as a function of time in NiO(001) excited with a $\lambda = 2933$ nm ($\hbar\omega_0 = 0.422$ eV, FWHM = 59 fs) laser pulse.

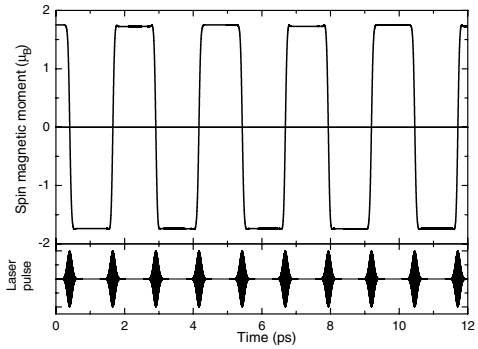

FIG. 3. Magnetic moment as a function of time in NiO(001) excited with a $\lambda = 963$ nm ($\hbar\omega_0 = 1.283$ eV FWHM = 115 fs) laser pulse.

Another absorption line in NiO(001) lies around 1.21 eV, as shown in Table I and in Fig. 1. This corresponds also to a mixture of $^1A_1$, $^3A_2$, and $^3B_2$ states. In this case, according to our results, the splitting of the states due to SOC is much smaller than in the previous one. Nevertheless, very good control of the spin state can be performed, as can be seen in Fig. 3 for a laser with a main frequency corresponding to transition (2) in Fig. 1 [29]. There we show a complete spin switching within 150 fs, which can be kept for much more than ten duty cycles.

It can be observed from our calculations that the state lasts more than 10 ps. Our model does not include phonons as a source of dephasing. Their inclusion should even improve our results, since once the barrier has been crossed, the phonons should make the system decay to the completely switched state. This should take a time of the order of the nanoseconds. This also improves the number of duty cycles, since the switching is complete, then constituting a new start of what we have shown in Fig. 3.

As the third case, another level of ^{3}E symmetry, is present at an energy of around 1.8 eV. The SOC splitting in this case is larger than in the previous two, allowing one to excite the different states quite selectively. The

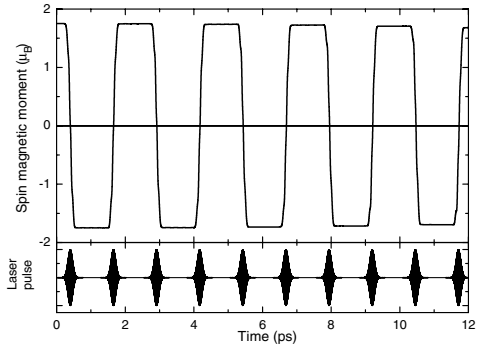

FIG. 4. Magnetic moment as a function of time in NiO(001) excited with a $\lambda = 752$ nm ($\hbar\omega_0 = 1.645$ eV, FWHM = 117 fs) laser pulse.

results obtained in this case are shown in Fig. 4 [30]. Again a switching is obtained within 150 fs, and the number of duty cycles is much more than ten.

In conclusion, the surface gap states of NiO(001), calculated by high-level *ab initio* quantum chemistry, have been employed to theoretically demonstrate, for the first time, all-optical spin switching on the subpicosecond time scale. The achieved switching does not depend on the symmetry of the electronic state or on the values of the energies used for the crystal field calculation. This opens up a new route to further theoretical as well as experimental investigations in order to determine the reliability of such an ultrafast all-optical switching and its technological applications.

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[1] Y. Acremann, C. H. Back, M. Buess, O. Portmann, A. Vaterlaus, D. Pescia, and H. Melchior, Science **290**, 492 (2000).
[2] J. P. Callan, A. M.-T. Kim, C. A. D. Roeser, E. Mazur, J. Solis, J. Siegel, C. N. Afonso, and J. C. G. de Sande, Phys. Rev. Lett. **86**, 3650 (2001).
[3] J. Siegel, C. N. Afonso, and J. Solis, Appl. Phys. Lett. **75**, 3102 (1999).
[4] E. Beaurepaire, J.-C. Merle, A. Daunois, and J.-Y. Bigot, Phys. Rev. Lett. **76**, 4250 (1996).
[5] J. Hohlfeld, E. Matthias, R. Knorren, and K. H. Bennemann, Phys. Rev. Lett. **78**, 4861 (1997).
[6] A. Scholl, L. Baumgarten, R. Jacquemin, and W. Eberhardt, Phys. Rev. Lett. **79**, 5146 (1997).
[7] E. Beaurepaire, M. Maret, and V. Halte, Phys. Rev. B **58**, 12 134 (1998).
[8] M. Aeschlimann, M. Bauer, S. Pawlik, W. Weber, R. Burgermeister, D. Oberli, and H. C. Siegmann, Phys. Rev. Lett. **79**, 5158 (1997).
[9] B. Koopmans, M. van Kampen, J. T. Kohlhepp, and W. J. M. de Jonge, Phys. Rev. Lett. **85**, 844 (2000).
[10] H. Regensburger, R. Vollmer, and J. Kirschner, Phys. Rev. B **61**, 14 716 (2000).
[11] R. Gómez-Abal and W. Hübner, Phys. Rev. B **65**, 195114 (2002).
[12] R. Gómez-Abal and W. Hübner, J. Phys. Condens. Matter **15**, S709 (2003).
[13] M. Edén, Y. K. Lee, and M. Levitt, J. Magn. Reson. A **120**, 56 (1996)
[14] W. Hübner and G. P. Zhang, Phys. Rev. B **58**, R5920 (1998).
[15] G. P. Zhang and W. Hübner, Phys. Rev. Lett. **85**, 3025 (2000).
[16] Note that switching of a quantum spin state involves its destruction, unlike the coherent rotation of a classical magnetization vector by a perpendicularly applied magnetic field pulse.
[17] A. K. Cheetham and D. A. Hope, Phys. Rev. B **27**, 6964 (1983).
[18] We performed density matrix calculations for a four-level model system including both population decay and dephasing. These calculations yield that the results are not affected if the decay or dephasing time constants exceed 1 ps. Thus, the relaxation to a bath is a small correction on the time scale of interest, or the notion of the bath is questionable. The neglect of additional interactions may limit the validity of our theory on longer time scales. However, our theory explores ultrafast switching in realistic systems and thus focuses on short time scales.
[19] A. Freitag, V. Staemmler, D. Cappus, C. A. Ventrice, Jr., K. Al-Shamery, H. Kuhlenbeck, and H.-J. Freund, Chem. Phys. Lett. **210**, 10 (1993).
[20] W. C. Mackrodt and C. Noguera, Surf. Sci. **457**, L386 (2000).
[21] M. Fiebig, D. Fröhlich, Th. Lottermoser, V. V. Pavlov, R. V. Pisarev, and H.-J. Weber, Phys. Rev. Lett. **87**, 137202 (2001).
[22] Electron energy loss spectra have been obtained for NiO(001) surfaces in B. Fromme, M. Möller, Th. Anschütz, C. Bethke, and E. Kisker, Phys. Rev. Lett. **77**, 1548 (1996).
[23] M. Trzeciecki, O. Ney, G. P. Zhang, and W. Hübner, Adv. Solid State Phys. **41**, 547 (2001).
[24] GAUSSIAN 98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople (Gaussian, Inc., Pittsburgh, PA, 1998).
[25] K. Satitkovitchai, Y. Pavlyukh, and W. Hübner, Phys. Rev. B **67**, 165413 (2003).
[26] No chirp has been taken into acount so far, but it can be done in a way similar to H. O. Jeschke, M. E. García, and K. H. Bennemann, J. Appl. Phys. **91**, 18 (2002).
[27] W. Hübner, K. H. Bennemann, and K. Böhmer, Phys. Rev. B **50**, 17 597 (1994).
[28] Maximum fluence of the laser pulse ≈ 6.9 J/cm^2.
[29] Maximum fluence ≈ 1.47 J/cm^2.
[30] Maximum fluence ≈ 1.49 J/cm^2.