Ultrafast Optical Pumping of Spin and Orbital Polarizations in the Antiferromagnetic Mott Insulators R_2CuO_4

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We demonstrate that optical pumping by circularly polarized light at the charge-transfer transition can induce spin and orbital polarizations in the strongly correlated Mott insulators R_2CuO_4 (R = Pr, Nd, Sm) providing a means of ultrafast nonlinear manipulation of spin states on time scales of less than 150 fs. We propose a model which includes both orbital- and spin-related processes possessing different spectral and temporal properties. This allows us to model the optical response of antiferromagnetic Mott insulators to circularly polarized light and estimate the spin relaxation time as $\tau_s \approx 30$–50 fs.

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Optical orientation is a physical phenomenon based on the transfer of angular momentum from circularly polarized light to matter. The principles of optical orientation were established by A. Kastler in his pioneering studies of paramagnetic atoms [1]. It allows one to disclose the basic processes which govern generation and relaxation of coherent spin states. Though the major physical mechanisms governing optical orientation in atoms, molecules, and semiconductors have been well established [2–4], it remains nowadays a focus of intense scientific research and technical application.

To the best of our knowledge all previous reports on optical orientation were devoted to magnetically *disordered* media. Strongly correlated Mott insulators belong to a large class of magnetically *ordered* materials characterized by high on-site Coulomb interaction and a complex interplay between spin, charge, and orbital degrees of freedom [5–8]. A strong enhancement of the nonlinear optical response in Mott insulators was predicted due to the interplay between the charge-transfer (CT) energy Δ_{CT} and the correlation energy U [9]. Other theories predict spin dynamics on time scales of 10–100 fs [10,11]. However, no experimental data on the spin dynamics at the CT transitions have been reported so far.

In this Letter, we report on the observation of ultrafast optical spin and orbital orientation and relaxation in the antiferromagnetic Mott insulators R_2CuO_4 which take place at time scales less than 150 fs. We show that the observed processes in these materials are fundamentally different from those in band semiconductors.

The rare-earth cuprates R_2CuO_4 (R = Pr, Nd, Sm) crystallize in the T' type tetragonal crystal structure $4/mmm$ [12,13]. The strong isotropic exchange interaction between the Cu^{2+} ions [electronic configuration $(3d)^9$, spin $S = 1/2$] leads to a two-dimensional antiferromagnetic ordering in CuO_2 planes, whereas the weak interplanar coupling results in a three-dimensional easy-plane antiferromagnetic ordering with a Néel temperature in the range of 250–320 K [14]. Optical responses of the T' type cuprates originate from the strongly coupled exciton related to the charge transfer from the fully occupied $(2p)^6$ oxygen shell into the empty $(3d)^9$ copper shell. This optical transition near 1.6 eV is well separated from the higher-energy continuum and has been evidenced by spectroscopic studies [15,16] and theoretically analyzed using different approaches [11,17–19].

Photoinduced rotation and ellipticity spectra were measured using a pump-probe technique [20,21]. A Ti:sapphire laser generating either ~1 ps or ~150 fs pulses at a repetition rate of 75.6 MHz in the energy range of 1.45–1.77 eV was used for excitation. The pump and probe beams were focused onto the sample surface to a spot of about 100 μm in diameter. The polished samples were prepared from flux-grown single crystals. The measurements were done from 8 up to 300 K.

The time-domain spectra were first measured in reflection at the (001)-plane of R_2CuO_4 (R = Pr, Nd, Sm) samples using 1 ps pulses. Figure 1 shows the photoinduced rotation for the photon energy range of 1.45–1.75 eV at zero pump-probe delay time. A Gaussian temporal behavior of the photoinduced optical rotation is observed for all excitation-photon energies (see example at 1.57 eV in the inset of Fig. 1). The spectra show a sign reversal for energies close to the electric-dipole CT transition around 1.6 eV [15,16]. By contrast, only very small signals were detected in a T-type La_2CuO_4 sample over the same energy range because in this material the CT transition occurs at 2.05 eV [15,16]. These observations undoubtedly show that the strong resonance enhancement of the photoinduced rotation and ellipticity in T'-type cuprates is due to the localized CT transitions. The photoinduced rotation is instantaneous within the ps pump pulse duration and there is no visible spin dynamics.

For revealing the intrinsic spin dynamics the laser pulse duration was reduced to 150 fs. Figures 2(a) and 2(b) show a typical temporal behavior of the photoinduced rotation

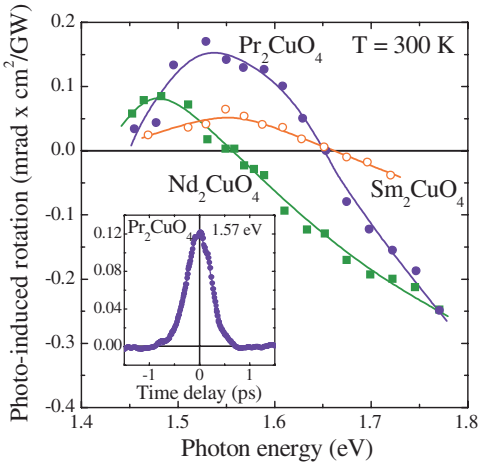

FIG. 1 (color online). Photoinduced optical rotation spectra in R_2CuO_4 (R = Pr, Nd, Sm) with 1 ps excitation at room temperature (points represent experimental data and lines are guides to the eye). Inset shows temporal behavior of the photoinduced optical rotation in Pr_2CuO_4.

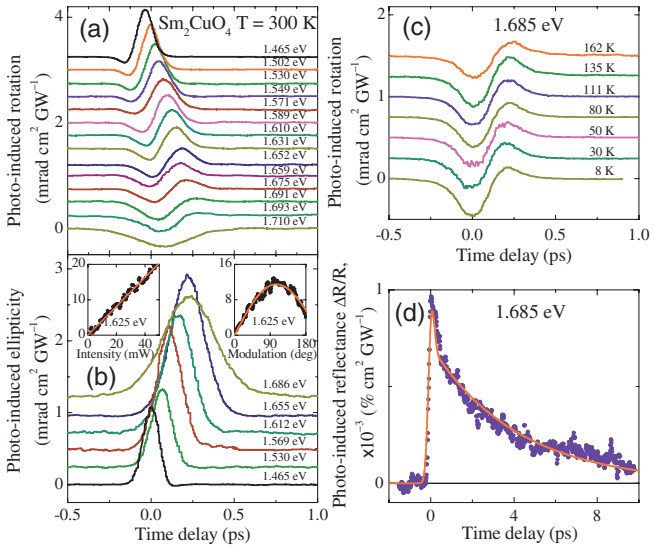

FIG. 2 (color online). Temporal behavior of the photoinduced (a),(c) rotation, and (b) ellipticity in Sm_2CuO_4 in the 150 fs pulse experiments. For clarity the traces have been shifted vertically. (a),(b) Temporal behavior of the photoinduced phenomena for different photon energies at room temperature. Insets in (b) show the changes of photoinduced ellipticity as a function of pump intensity (left panel) and modulation degree of the pump beam by a photoelastic modulator (right panel). Experimental data in these insets (points) were fitted by a linear function (left panel) and a Bessel function of second order (right panel), fits are shown by lines. (c) Temporal behavior of the photoinduced rotation at low temperatures. (d) Temporal behavior of the photoinduced reflectance in Sm_2CuO_4 in the 150 fs pulse experiments.

and ellipticity measured at room temperature on the $Sm_2CuO_4(001)$ sample. In contrast to the 1 ps pulse experiments, systematic changes are observed in temporal behavior and intensity when scanning the pump energy across the CT resonance. Note, in particular, that the temporal response is no longer Gaussian. The rotation changes sign near by zero time delay, whereas the ellipticity does not. Thus, the spin-related dynamics takes place on time scales shorter than 150 fs. Figure 2(c) shows data for the photoinduced rotation as a function of temperature. Only small changes related to the temperature-induced shift of the 1.6 eV absorption band are observed.

In order to confirm that the photoinduced rotation is due to spin-related phenomena, we studied the temporal behavior of the pump-induced reflectivity which is a charge-related property. The results for the Sm_2CuO_4 sample measured by using linearly polarized light are shown in Fig. 2(d). They reveal a charge-relaxation dynamics in which nonradiative recombination processes play a dominant role. Obviously the charge dynamics takes place on a picosecond time scale with $\tau_1 \approx 4$ ps and is essentially longer than the spin dynamics.

The most important issues to be discussed now are the electronic and magnetic structures which govern photoinduced spin-related phenomena in solids [22]. The processes of ultrafast optical excitation and relaxation in the Mott insulators R_2CuO_4 are radically different from those in ferromagnetic metals; therefore, we discuss them by comparing cuprates with semiconductors. In semiconductors such as GaAs, the $4p$-type valence band is subject to a strong spin-orbit splitting, whereas the $4s$-type conduction band has zero angular momentum [3,4]. Cuprates have a $2p$-type valence oxygen band and the charge-transfer transitions occur into the empty copper $3d_{x^2-y^2}$ band [17,18]. These bands are subject to the crystal-field, the spin-orbit, and the exchange splittings.

It is well established that the low-energy optical excitation in the cuprates stems from the CT transitions and the theoretical description of their optical properties requires accounting for the strong electron correlations. This can be done using different models [11,17–19]. The analysis of optical absorption data shows that for this purpose one can use a single-cluster excitonic model which takes into account most of the essential effects of correlations [17,18]. However, the spin-orbit coupling, which is of principal importance for analysis of optical orientation, was not taken into account in previous studies. Figure 3 is a single-hole representation of the energy levels for a CuO_4 cluster where we took into account the tetragonal crystal-field splitting and spin-orbit interaction. Only the ground b_{1g}^b copper state and the excited e_u^b oxygen states are shown. Orbital $(x^2 - y^2)$, $1/\sqrt{2}(x \pm iy)$ and spin $\uparrow, \downarrow$ parts of the wave functions are given accounting for crystal-field splitting, the spin-orbit, and exchange interaction. The excited state e_u^b is split by the spin-orbit interaction Δ_{so} into two double-degenerate levels, labeled by their irreducible representations Γ_6^- and Γ_7^- with total angular-momentum projections onto the z axis $m_j = \pm 1/2$ and $\pm 3/2$, respectively. The hole ground-energy state Γ_7^+ is characterized by spin components $S_x = \pm 1/2$ along the in-plane anisotropy field.

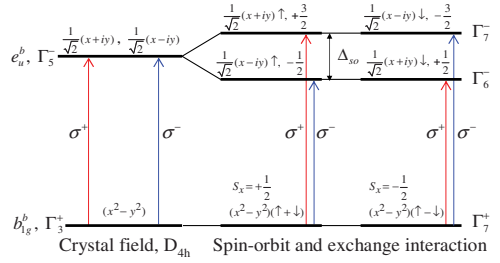

FIG. 3 (color online). Schematic energy-level diagram and selection rules for dipole-allowed optical CT transitions within a CuO_4 plaquette with D_{4h} symmetry. Two states are shown for two neighboring Cu^{2+} ions with $S_x = +1/2$ and $S_x = -1/2$. Notations of levels are according to Ref. [29].

Several important conclusions can be drawn from this energy-level diagram. First, even if the spin-orbit splitting is neglected, optical orientation would take place because the CT transition is electric-dipole-allowed and the projection of the angular-momentum m_j is changed from 0 to ± 1. This process is related with the orbital excitation of electrons. The coherence of electrons is lost almost instantaneously with a time τ_2 on the order of 10 fs due to the strong electron-phonon interaction (a rough estimate can be done from the band width of the relevant electronic transition). No sign change of the induced rotation is expected for the orbital contribution when scanning the pump across the resonance. The involvement of the spin-orbit splitting is essential for understanding the spin orientation. In contrast to the orbital part the spin contribution to the optical orientation changes sign when scanning the photon energy of the σ^+ or σ^- pump beam through the CT resonance, for example, from Γ_6^- to Γ_7^-. During this process a hole from a copper $Cu^{2+}(3d)^9$ ion moves onto the oxygen $O^{2-}(2p)^6$ ion. The diagram shown in Fig. 3 for the CT transition $b_{1g}^b \rightarrow e_u^b$ is in good agreement with 100% polarized optical absorption spectra for linearly polarized light [16] and optical orientation for circularly polarized light, as seen in our experiments.

Another factor that noticeably distinguishes cuprates from semiconductors lies in their magnetic structures. Spins in semiconductors are delocalized, the spin structure is fully disordered, and the process of optical orientation is isotropic. By contrast, spins at the copper sublattices are localized. Moreover, in the antiferromagnets the magnetic anisotropy is always strong. Figure 3 shows that two $S_x = +1/2$ and $S_x = -1/2$ antiferromagnetically coupled CuO_4 clusters contribute constructively to optical orientation for light propagating along the z axis.

The distinct differences between cuprates and semiconductors must obviously lead to different time scales of the relaxation processes. In semiconductors, the hole spin relaxation occurs on time scales of 100 fs [23], whereas electron spin relaxation typically occurs on much longer time scales [4]. The CT transitions in cuprates lead to the formation of strongly coupled small-sized excitons, comprising the neighboring nonmagnetic $Cu^{1+}(3d)^{10}$ ions and the magnetic $O^{1-}(2p)^5$ ions. These "CuO molecules" are subject to a strong exchange field of the neighboring $Cu^{2+}(3d)^9$ ions. Moreover, the spin-phonon interaction is significant in cuprates [24]. All these factors favor a fast spin relaxation dynamics.

Now we proceed with an estimate of the relaxation times from the experimental data. To describe quantitatively the optical response, the semiconductor Bloch equations have to be solved [25]. Important parameters are the charge-relaxation time τ_1, the charge decoherence time τ_2, and the spin relaxation time τ_s. The relation $\tau_2 \ll \tau_s \ll \tau_1$ between these values allows us to simplify the problem. Assuming that the pump and probe pulses have Gaussian temporal behavior, the photoinduced rotation θ_K, and ellipticity ϵ_K can be analyzed by [21,23]:

$$\theta_K + i\epsilon_K = \frac{A}{\sigma\sqrt{\pi}} \exp\left(-\frac{\tau^2}{\sigma^2}\right) + \frac{B}{2} \exp\left(-\frac{\tau}{\tau_s} + \frac{\sigma^2}{4\tau_s^2}\right) \times \left[1 - \mathrm{erf}\left(\frac{\sigma}{2\tau_s} - \frac{\tau}{\sigma}\right)\right], \quad (1)$$

where τ is the pump-probe time delay and σ is the width of the Gaussian pulse. The first and second terms in Eq. (1) describe instantaneous orbital and noninstantaneous spin contributions, respectively. The noninstantaneous contribution is related to ultrafast optical orientation with the spin relaxation time τ_s. The coefficients in Eq. (1) are related to the dielectric function as A, $B \propto -i\varepsilon_{xy}^{\mathrm{orbit,spin}} / \varepsilon_0^{1/2}(\varepsilon_0 - 1)$, where $\varepsilon_0 = \varepsilon_{xx} = \varepsilon_{yy}$ and $\varepsilon_{xy}^{\mathrm{orbit,spin}}$ are complex diagonal and photoinduced off-diagonal parts of the dielectric function, respectively. The spectral behavior of orbital and spin contributions discussed above on the basis of the energy-level diagram corresponds to two basic cases of electronic transitions which have been analyzed in [26].

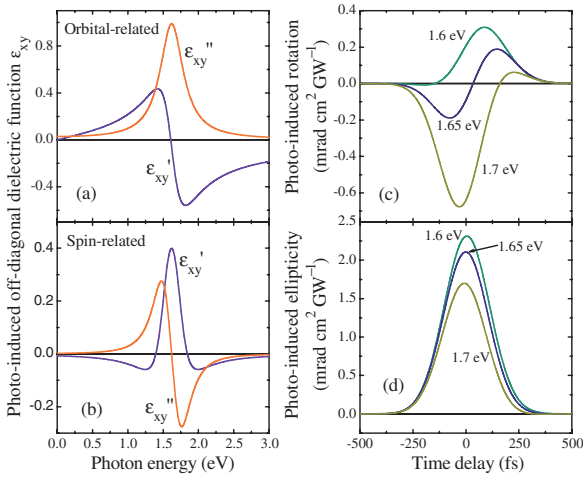

FIG. 4 (color online). Spectral behavior of the off-diagonal dielectric functions for (a) the orbital-related and (b) the spin-related contributions calculated on the basis of Eqs. (36) and (32) in [26]. Temporal variation of (c) the photoinduced rotation and (d) ellipticity for three different photon energies calculated on the basis of Eq. (1).

These two types are often called diamagnetic absorption-like and paramagnetic dispersionlike behaviors [27].

Using Eq. (1) and applying a fit to the experimental data we have estimated the spin relaxation time as $\tau_s \approx$ 30–50 fs. For this purpose a Fortran program based on the Levenberg-Marquardt algorithm was used. The values of spin relaxation time are within the time scales of 10–100 fs predicted theoretically for the Mott insulators [10,11]. Figure 4 shows the simulated spectral behavior of the off-diagonal dielectric functions for the orbital-related and the spin-related contributions, and the temporal variation of the photoinduced rotation and ellipticity in Sm_2CuO_4. For modeling we used literature data on the diagonal dielectric function with the respective spectral shape [16]. Further we used a CT transition energy $E_0 =$ 1.62 eV, a damping energy $\Gamma_0 = 0.2$ eV, a Gaussian pulse time duration width $\sigma = 150$ fs, an estimated spin relaxation time $\tau_s = 40$ fs and a spin-orbit splitting $\Delta_{so} =$ 0.1 eV. Good qualitative agreement between the measured experimental data in Figs. 2(a) and 2(b) and calculated ultrafast optical responses in Figs. 4(c) and 4(d) is found. Some discrepancy may arise due to (i) extrinsic reasons, e.g., dispersion in the optical elements of the experimental setup gives rise to a spectral broadening and relative time shift of the laser pulses, and (ii) intrinsic reasons due to a possible contribution of the parity-forbidden *d*-*d* and CT transitions at higher energies [18]. The orbital- and spin-related contributions were found to have comparable magnitudes. We relate this to the strong optical nonlinearities of the parity-allowed CT transition $b_{1g}^b \rightarrow e_u^b$ to an orbitally degenerate state.

To conclude, we have demonstrated ultrafast optical spin and orbital orientation and relaxation at the charge-transfer transitions in the strongly correlated Mott insulators R_2CuO_4. We propose a model which includes both orbital- and spin-related processes possessing different spectral and temporal properties. This allows us to model the optical response of Mott insulators to circularly polarized light and estimate the spin relaxation time as $\tau_s \approx$ 30–50 fs due to the strong spin-orbit coupling, spin-phonon, and exchange interactions within the CuO_2 planes. Mott insulators possess a rich variety of electronic and magnetic structures and further experiments will reveal novel photoinduced spin and orbital optical phenomena. Aside from the new physics related to ultrafast nonlinear optics, the high values of the spin-related optical effects comparable to those in model semiconductors and dielectrics [20,21,28] may have significant impact and potential for future all-optical technologies.

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