Time-resolved nonlinear optical spectroscopy of Mn^{3+} ions in rare-earth hexagonal manganites $R\,MnO_3$ ($R=$ Sc, Y, Er)

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A time-resolved, spectroscopic study of the third-order nonlinear optical response of rare-earth hexagonal manganites $R\,MnO_3$ ($R=$ Sc, Y, Er) was performed in the range of 1.45 to 1.62 eV nearby the first $d-d$ transition in Mn^{3+} ions. The nonlinearity was shown to result in a transient perturbation $\Delta\varepsilon(\omega)$ of the dielectric permittivity tensor, whose antisymmetric part decays within less than 100 fs through the relaxation of excited electrons. The symmetric part of $\Delta\varepsilon(\omega)$ was found to depend upon two distinct relaxation processes with decay times of about 360 fs and more than 70 ps, which were attributed to phonon thermalization and lattice cooling, respectively.

Time-dependent optical phenomena related to the third-order nonlinear susceptibility $\chi^{(3)}$ of materials attract much interest because of their importance for applications such as ultrafast optical switching.[1,2] Transition metal oxides manifest a large $\chi^{(3)}$ in the spectral range where their absorption is dominated by $d-d$ and near-bandgap transitions. Recently, transition metal oxides such as α-Fe_2O_3, γ-Fe_2O_3, or Fe_3O_4 have been found to present some of the highest values (10^{-10}–10^{-9} esu) of $\chi^{(3)}$ among inorganic compounds.[3] However, while one of the main purposes of the enhancement of the third-order nonlinear susceptibility is the realization of fast optical switching, to the best of our knowledge, no time-resolved study of the nonlinear optical phenomena in these materials has been performed as yet. Moreover, the study of $\chi^{(3)}$ in transition metal oxides has not been much extended to species other than the simple oxides mentioned above.

Rare-earth (R) manganites $R\,MnO_3$ form a broad class of transition metal oxides exhibiting a wide range of exotic galvanomagnetic, magnetic, electronic, and optical properties.[4] The huge interest for this family of strongly correlated systems has mostly been focused on orthorombic manganites, which exhibit giant magnetoresistivity. Only recently was some attention devoted to hexagonal manganites. Their linear and nonlinear optical properties are of particular interest from both an experimental[5–8] and a theoretical point of view.[9–11] Up to now, though, no time-resolved analysis of their nonlinearities was performed, although this would provide new fundamental information about their nonequilibrium electronic and optical properties. We report here on a temporal and spectroscopic optical study of three hexagonal manganites, $ScMnO_3$, $YMnO_3$, and $ErMnO_3$.

Intense light excitation modifies the optical properties of a medium, which in turn can affect the properties of light itself. This can be used for all-optical studies in a two-beam configuration, in which an intense (pump) light beam excites the medium and a less intense (probe) beam monitors the pump-induced nonlinear changes of its properties. In such a configuration, the nonlinearity can be expressed through the third-order nonlinear polarization vector $\mathbf{P}^{(3)}(\omega)$ arising from the interaction of the pump $\mathbf{E}(\omega)$ and probe $\mathbf{e}(\omega)$ electric fields:

$$P_i^{(3)}(\omega)=\chi_{ijkl}^{(3)}(-\omega;\omega,\omega,-\omega)e_j(\omega)E_k(\omega)E_l^*(\omega), \quad (1)$$

where $\chi_{ijkl}^{(3)}$ is the static third-order nonlinear susceptibility of the material. Equation (1) can be rewritten as a relation between the pump-induced perturbation of the dielectric permittivity tensor $\varepsilon(\omega)$ and the nonlinear susceptibility tensor $\chi^{(3)}$:

$$\Delta\varepsilon_{ij}(\omega)=\chi_{ijkl}^{(3)}(-\omega;\omega,\omega,-\omega)E_k(\omega)E_l^*(\omega). \quad (2)$$

The product $E_k(\omega)E_l^*(\omega)$ can be conveniently decomposed into a symmetric and an antisymmetric part with respect to permutations of the indices k and l. The symmetric part is real and nonzero when the pump is linearly polarized, while the antisymmetric part is imaginary and nonzero when the pump beam is circularly polarized. The tensor $\Delta\varepsilon_{ij}$ itself comprises a symmetric $\Delta\varepsilon_{ij}^s$ and an antisymmetric $\Delta\varepsilon_{ij}^a$ part with respect to permutations of the indices i and j.[12] The nonlinearities resulting in $\Delta\varepsilon_{ij}^s$ and $\Delta\varepsilon_{ij}^a$ can be shown to be determined by the real and imaginary parts of $E_k(\omega)E_l^*(\omega)$, respectively.

In the following we discuss the spectral and temporal behavior of the optical nonlinearities due to $d-d$ transitions in the Mn^{3+} ions of hexagonal manganites. Their electronic structure has only very recently become a subject of theoretical studies. For example, calculations based on different approximations predicted $YMnO_3$ to be a charge–transfer insulator with a bandgap of 1.1 eV,[10] or a semiconductor with a bandgap of about 1.5 eV.[11] Although reported experimental data[5,7] are close to the theoretical estimates, the assignment of the strong absorption in this spectral range to an interband or a charge–transfer transition remains controversial.

Recently, though, a new interpretation of the optical properties of hexagonal manganites was proposed.[8] Figure 1 shows their electronic energy diagram as derived from the local symmetry of the Mn^{3+} ion. Without crystalline field,
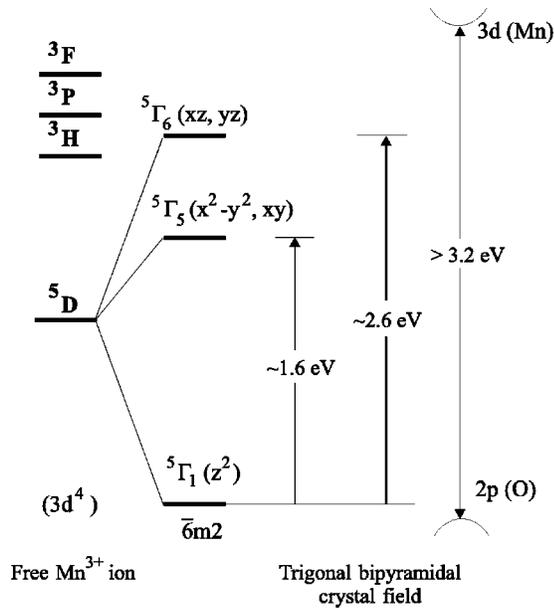
FIG. 1. Energy level scheme of hexagonal manganites.

the four $3d$ electrons of the free Mn^{3+} ion ($3d^4$ configuration) occupy the ground state ^5D ($L=2$, $S=2$) which is a quintet state. In an hexagonal manganite the ^5D state splits into a $^5\Gamma_1$ ground state and two excited $^5\Gamma_5$ and $^5\Gamma_6$ states under the influence of a moderate crystalline field resulting from the trigonal bipyramidal symmetry $\bar{6}m2$. The overall splitting is approximately 2.6 eV, including the d–d transition $^5\Gamma_1(t_2^3e^1) \rightarrow {}^5\Gamma_5(t_2^2e^2)$ at 1.6 eV.[13] Charge–transfer transitions between O $2p$ and Mn $3d$ are expected to occur above 3 eV,[7] i.e., far above the 1.1–1.5 eV predicted by the aforementioned theoretical calculations.[10,11] Hexagonal manganites are transparent below 1.3–1.5 eV down to about 0.1 eV, where phonon absorption starts to rise.[14,15]

The samples investigated for this study are [0001]-oriented single crystals grown from high temperature solutions in a PbO-PbF$_2$ flux. The optical measurements were performed in a pump and probe configuration, using a pulsed Ti:sapphire laser with a pulse duration of approximately 100 fs and a repetition rate of 82 MHz in the photon energy range of 1.45–1.62 eV.
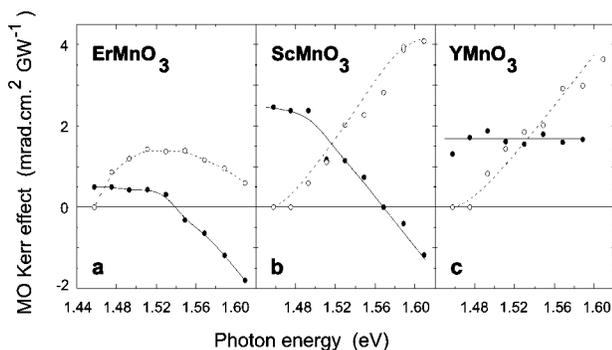

FIG. 2. Spectral dependences of the photo-induced magneto-optical Kerr rotation (full circles) and ellipticity (open circles) in (a) ErMnO$_3$, (b) ScMnO$_3$, and (c) YMnO$_3$. Lines are guides to the eye.

The *antisymmetric* nonlinear perturbation $\Delta\varepsilon_{ij}^a(\omega)$ of the dielectric permittivity tensor $\varepsilon(\omega)$ is deduced from the pump-induced magneto-optical Kerr effect experienced by the probe beam. The setup for time-resolved magneto-optical Kerr effect measurements was described in detail elsewhere.[16] The polarization of the circularly-polarized pump beam was modulated between left-handed and right-handed helicities, while the probe was s-polarized. Both beams were focused on the sample to a spot diameter of about 100 μm for the pump pulse and slightly less for the probe pulse. The pump fluence on the samples was around 10 μJ cm^{-2}. The Kerr rotation and ellipticity experienced by the probe beam were measured as a function of the time delay τ_d between pump and probe pulses, with a sensitivity as high as 0.2 μrad. The spectral width of the pulses, monitored with an optical multichannel analyzer, was about 0.02 eV over the whole photon energy range.

The behavior of the the *symmetric* nonlinear perturbation $\Delta\varepsilon_{ij}^s(\omega)$ of the permittivity tensor $\varepsilon(\omega)$ is also deduced from the rotation of the probe polarization plane upon reflection from the sample. The same setup as described above is used, with the exception that the incoming probe polarization is set to 20° from the s direction, whereas the pump pulses are linearly s-polarized but modulated in intensity. The rotation experienced by the probe beam, measured as a function of τ_d, is due to the nonmagnetic, third-order nonlinear optical Kerr effect.[17] In order to avoid confusion between the photo-induced magneto-optical Kerr effect and the optical Kerr effect, the latter will be described in the following as a photo-induced "birefringence."

The spectral behavior of the photo-induced magneto-optical Kerr effect at $\tau_d=0$ is shown in Figs. 2(a), (b), and (c) for ErMnO$_3$, ScMnO$_3$, and YMnO$_3$, respectively. A maximum of the Kerr ellipticity and a zero of the Kerr rotation are observed approximately at the same photon energy in ErMnO$_3$ [Fig. 2(a)]. The spectral dependence for ScMnO$_3$ [Fig. 2(b)] and YMnO$_3$ [Fig. 2(c)] is similar, provided a shift towards lower photon energies is performed, and is typical of the photo-induced magneto-optical Kerr effect in the case of a two-level system in which an energy splitting of the spin sublevels exists.[16,18]

The electronic energy diagram of Mn^{3+} ions, together with those spectral shapes and the fact that comparable values of the Kerr effect were measured in all three materials, suggest that, within the studied spectral range, the observed nonlinear optical properties are determined by the d–d transition $^5\Gamma_1 \rightarrow {}^5\Gamma_5$ in Mn^{3+} ions. The transition energy varies slightly from compound to compound, which can be explained by the difference in their crystalline fields. The spectrum of ErMnO$_3$, with a transition energy markedly apart from that observed for the two other compounds, can be accounted for by an additional transition $^4I_{15/2} \rightarrow {}^4I_{9/2}$ in Er^{3+} ions that takes place at ~ 1.525 eV.[19]

The dependence of the Kerr ellipticity upon τ_d is shown in Fig. 3 for ErMnO$_3$. The signal is nonzero only over the time domain of the cross correlation function $\mathcal{C}(t)$ of pump and probe pulses. A similar temporal behavior is observed for the Kerr rotation. Figure 3 also presents the polarization
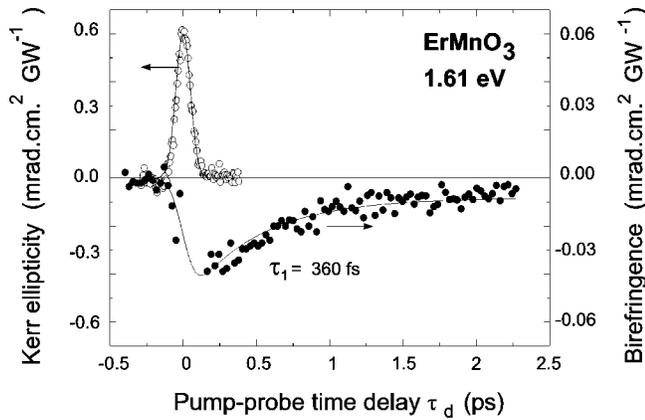
FIG. 3. Temporal dependences of the photo-induced magneto-optical Kerr ellipticity (open circles) and birefringence (solid circles) in ErMnO$_3$ at 1.61 eV. Lines are fits based on Eq. (3).

rotation due to the photo-induced ''birefringence,'' whose temporal behavior, in contrast to that of the magneto-optical Kerr effect, can clearly be decomposed into a fast initial peak and a slower relaxing part. By $\tau_d = 2$ ps the relaxation has been completed and the signal reaches a plateau, without further change during the following 70 ps. It should be mentioned that this photo-induced birefringence also contains a coherent peak within the duration of $\mathcal{C}(t)$, but for clarity this contribution is not shown. The data can be fitted neglecting this instantaneous coherent contribution and the best fits are obtained considering two relaxation components:[18]

$$\theta_K = \frac{B}{2} \exp\left(\frac{w^2}{\tau_1^2} - \frac{\tau_d}{\tau_1}\right) \left[1 - \mathrm{erf}\left(\frac{w}{\tau_1} - \frac{\tau_d}{2w}\right)\right]$$
$$+ \frac{C}{2} \exp\left(\frac{w^2}{\tau_2^2} - \frac{\tau_d}{\tau_2}\right) \left[1 - \mathrm{erf}\left(\frac{w}{\tau_2} - \frac{\tau_d}{2w}\right)\right], \quad (3)$$

where w is the rms width of the pulses. The two relaxing terms of amplitudes B and C have relaxation times τ_1 and τ_2, respectively. The parameters $w = 50$ fs and $\tau_2 \gg w$ were set as fixed, while B, C, and τ_1 were the fitting parameters. The fitting procedure produced an estimated $\tau_1 = 360 \pm 40$ fs.

Notice that no signal was observed when the linear polarization of the probe beam was set to s, while the polarization of the pump beam was tilted from its initial s orientation by an angle of 20°. This suggests that the temporal behavior of the photo-induced ''birefringence'' shown above is largely dominated by isotropic changes in the refraction index itself.

Under the assumption that light reflection from the crystal surface is determined by the real part of the refractive index n, the amplitudes B and C deduced from the fitting procedure were expressed in terms of the differential refractive index $\Delta n/n$, as presented in Fig. 4 for ErMnO$_3$. This transformation was done assuming $n = 2.01$ over the whole studied spectral range.[20] Notice that the absolute sign of the photo-induced ''birefringence'' cannot be deduced from our measurements. Consequently, the corresponding photo-refraction and its characteristic amplitudes B and C are shown with an inherent uncertainty about their signs. Clearly, though, B and
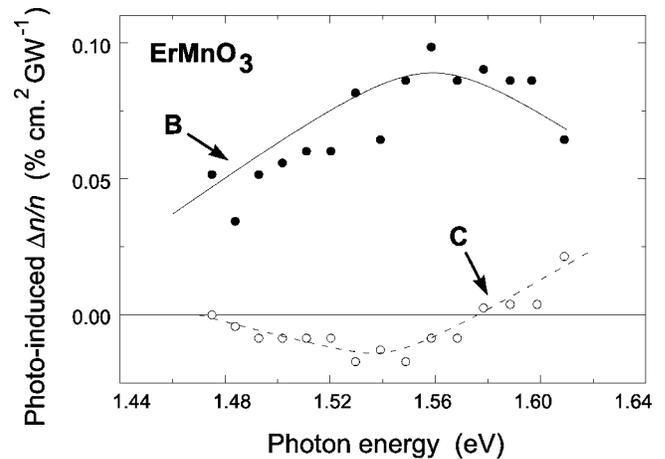

FIG. 4. Spectral dependences of B and C, amplitudes of the relaxing contributions to the photo-induced differential refractive index of ErMnO$_3$. Lines are guides to the eye.

C have different spectral dependences. The amplitude B of the fast relaxing contribution shows a maximum at the energy of the transition $^5\Gamma_1 \rightarrow {}^5\Gamma_5$ in Mn^{3+} ions (see Fig. 1), whereas the amplitude C of the slowly relaxing part changes sign at approximately the same energy. From the maximum value reached by the amplitude B of the fast component within the experimental spectral range, we could estimate the maximum of the relevant third-order susceptibility $\chi^{(3)}$ of ErMnO$_3$ to be of the order of 2×10^{-9} esu.

Absorption spectra of hexagonal manganites show that the spectral line of the $^5\Gamma_1(t_2^3 e^1) \rightarrow {}^5\Gamma_5(t_2^2 e^2)$ transition in Mn^{3+} ions is rather broad,[7,8] which is usually attributed to an electron–phonon interaction, i.e., the fact that the transition of an electron towards an excited state is accompanied by the radiation of an optical phonon. Clearly, the very large spectral linewidth reported in literature cannot be related to inhomogenous broadening.[13] Moreover, the studied transition takes place between states of different electronic configuration, and is therefore intrinsically broad.[9,13] Thus the lifetime of the electron in the excited state cannot exceed much a few tens of femtoseconds. Therefore, in our experiment, the associated photo-induced magneto-optical Kerr effect is not expected to be observed for pump-probe time delays τ_d longer than the duration of the pump-probe cross correlation function $\mathcal{C}(t)$. Nevertheless, whereas excited electrons relax very fast indeed, the medium remains in an excited state because of the generation of phonons through electron–phonon interactions and nonradiative relaxation of electrons from the excited to the ground state. The complex refraction index should be sensitive to this nonequilibrium state. Thus the temporal behavior of the photo-induced ''birefringence'' is driven by the dynamical phenomena involving phonons.

Although a detailed explanation of this dynamical behavior is beyond the scope of this paper, we can nevertheless propose a simple model to describe the observed spectral dependences. The spectral dependence of the refraction index within a given energy range comprising only one electronic transition can be presented as the sum of an energy-independent contribution resulting from all electronic

transitions outside the considered spectral range and of a contribution resulting from the transition within this range. The latter depends on photon energy and is characterized by an s-like spectrum. In the frame of this model, the fast relaxing component arises from photo-induced changes of the energy-independent part of the signal, i.e., it is mostly due to spectral changes outside the considered energy range. A spectral maximum of the fast relaxing contribution within this range shows that the initial optical excitation of the system consists of $^5\Gamma_1 \to {}^5\Gamma_5$ transitions in Mn^{3+} ions. On the other hand, the slowly relaxing component shows a distinctive dispersion mostly conditioned by effective changes of the spectral weight of the resonant $^5\Gamma_1 \to {}^5\Gamma_5$ transition. The drastic changes of the $\Delta n/n$ spectrum within the first 1.5 ps strongly suggest rapid variations of the phonon distribution function. The fast relaxation can therefore be attributed to phonon thermalization through the anharmonic decay of optical phonons. From experimental Raman scattering data one can estimate that this decay takes place within approximately 500 fs.[15] This is in good agreement with the value obtained in this work (360 ± 40 fs). When this rapid thermalization process is completed, the excitation of the system manifests itself through an increased phonon temperature. Although the temperature increase influences all optical transitions, the contributions from transitions other than $^5\Gamma_1 \to {}^5\Gamma_5$ are blurred as a consequence of dispersion. Therefore the slow relaxation is related to lattice cooling.

In summary, a time-resolved spectral study of the third-order nonlinear optical response of rare-earth hexagonal manganites was performed. The observed spectral resonances were attributed to $d-d$ transitions $^5\Gamma_1 \to {}^5\Gamma_5$ in Mn^{3+} ions. The nonlinearities exhibited by these systems, found to be of the order of 2×10^{-9} esu, are on a par with the largest values measured in other inorganic compounds. The decay of the nonlinearity resulting in an antisymmetric perturbation $\Delta \varepsilon_{ij}^a$ of the dielectric permittivity tensor was shown to be conditioned by the relaxation of the excited electrons. The nonlinear symmetric perturbation $\Delta \varepsilon_{ij}^s$ of the tensor extends over a longer time span, and experiences a drastic change of its spectral dependence within the first 1.5 ps, the analysis of which led us to attribute its decay to both phonon thermalization and lattice cooling.

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