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## Optical second- and third-harmonic generation on the ferromagnetic semiconductor europium oxide

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Optical second- and third-harmonic generation on epitaxial films of the ferromagnetic semiconductor europium oxide reveal selective coupling to the magnetic and crystallographic properties of the compound. Second-harmonic generation couples linearly to the order parameter parametrizing the long-range ferromagnetic order. In contrast, third-harmonic generation couples to the crystallographic lattice and to the short-range spin-spin correlations manifesting macroscopically as a magnetostrictive effect. These results demonstrate the potential of nonlinear optics for acquiring unique information about the crystallographic, electronic, and magnetic properties of spintronics compounds. © 2011 American Institute of Physics. [doi:10.1063/1.3540685]

### I. INTRODUCTION

The ferromagnetic semiconductor europium oxide (EuO) has recently been attracting a renewed interest for spintronics applications.<sup>1,2</sup> From a historical point of view, in addition to a multitude of extraordinary spin-related transport properties,<sup>3-5</sup> many remarkable optical and magneto-optical properties have been revealed, such as a strong linear and circular birefringence/dichroism<sup>6-8</sup> and a large red shift of the absorption edge.<sup>9</sup> These observations have aroused intensive experimental and theoretical studies in close relation with the elucidation of the anomalous transport properties. Nevertheless, nonlinear optical effects, which are associated with higher order optical susceptibilities, have never been reported for EuO, until very recently.<sup>10</sup> This is possibly due to its centrosymmetric crystal structure which forbids the optical second-harmonic generation (SHG) as the leading-order nonlinear process. Because nonlinear optics has great potential to disclose the microscopic mechanisms of light-matter interaction and to get unique information about the crystallographic, electronic, and magnetic structure including states that are inaccessible by linear optics,<sup>11,12</sup> the investigation of the nonlinear optical properties of EuO is of special interest.

Here we report the second- and third-order optical response of epitaxial EuO films. It is shown that the former is magnetic-dipole (MD) induced and probes the long-range ferromagnetic order, while the latter is electric-dipole (ED) induced and reflects short-range spin correlations. Thus, nonlinear optics provides a versatile tool in the process of understanding the multiple anomalous properties in this compound.

EuO has a centrosymmetric cubic rock salt structure (point group  $m3m$ ). It undergoes a ferromagnetic transition at  $T_C = 69$  K. The  $\text{Eu}^{2+}$  ions have localized  $4f^7$  electrons with  $^8S_{7/2}$  as the ground state.

In the majority of cases, SHG is applied to noncentrosymmetric materials or to the surface or interface of centrosymmetric materials where the inversion symmetry is locally broken and the strongest interaction by the ED transitions is expected.<sup>11,12</sup> In centrosymmetric systems, SHG is only allowed if higher-order multipole contributions in the expansion of the electromagnetic light field such as MD or electric-quadrupole (EQ) contributions are involved. In EuO this leads to<sup>13,14</sup>

$$P_i(2\omega) = \varepsilon_0(\chi_{ijk}^{(i)} + \chi_{ijk}^{(c)})E_j(\omega)H_k(\omega), \quad (1)$$

where the time-invariant ( $i$ -type) tensor  $\chi_{ijk}^{(i)}$  and the time-noninvariant ( $c$ -type) tensor  $\chi_{ijk}^{(c)}$  are the second-order nonlinear susceptibilities related to, in the leading order, crystallographic SHG and magnetization-induced SHG, respectively.  $E_j(\omega)$  and  $H_k(\omega)$  in Eq. (1) denote the  $j$ -polarized electric field ( $\sim$ ED) and the  $k$ -polarized magnetic field ( $\sim$ MD) of the fundamental light, respectively, that induce the  $i$ -polarized SHG wave  $P_i(2\omega)$  ( $\sim$ ED).

In contrast, all ED-type third-harmonic generation (THG) is allowed in centrosymmetric materials. This is expressed by

$$P_i(3\omega) = \varepsilon_0(\chi_{ijkl}^{(i)} + \chi_{ijkl}^{(c)})E_j(\omega)E_k(\omega)E_l(\omega), \quad (2)$$

where  $i$ -type tensor  $\chi_{ijkl}^{(i)}$  and  $c$ -type tensor  $\chi_{ijkl}^{(c)}$  are the third-order nonlinear susceptibilities related to crystallographic and magnetic THG, respectively.

The EuO films are probed with light incident along one of the principal axes ( $k \parallel z$ ) with the spontaneous magnetization parallel to the  $y$  direction. For this configuration, the non-zero tensor components for bulk MD-SHG and bulk ED-THG are summarized in Table I.<sup>15</sup> Clearly, any  $i$ -type SHG and  $c$ -type THG are zero so that it is expected that SHG and THG allow us to distinguish between optical contributions of magnetic and nonmagnetic origin in a convenient way.

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Epitaxial EuO (001) films protected by an amorphous silicon (a-Si) cap layer of 10 nm were grown on a two-sided polished YAlO<sub>3</sub> (110) substrate by molecular-beam epitaxy.<sup>1</sup> For most of the measurements, films with a thickness of 100 nm were used. The detailed experimental technique is described elsewhere.<sup>10</sup> For the SHG and THG measurements, a regenerative Ti:sapphire amplifier system with a central wavelength of 800 nm (1.55 eV), a pulse width of 120 fs, and a repetition rate of 1 kHz was used as the light source. The EuO sample was excited by light with a photon energy of 0.67–1.56 eV generated by an optical parametric amplifier. The SHG and THG signals were measured in transmission geometry in an external magnetic saturation field of 0.1 T applied in the Voigt configuration ( $H \parallel y$ ), as shown in the inset of Fig. 1.

Figure 1 shows the SHG spectra from  $\chi_{xxy}$  and  $\chi_{xyx}$  at 10 K. Although ED-SHG is forbidden, due to the centrosymmetry, a pronounced SHG signal is observed. It is therefore associated to MD-SHG according to Eq. (1). It should be noted that surface-induced noncentrosymmetric ED-SHG leads to the same polarization selection rules as bulk-induced centrosymmetric MD-SHG.<sup>15</sup> However, the linear dependence of the SHG intensity on the thickness of the EuO film in the inset of Fig. 1 confirms that SHG in EuO is described by the bulk-induced MD process. The resonant enhancement of the SHG signal below  $2\hbar\omega = 2.5$  eV coincides with the  $4f^7 \rightarrow 4f^6 5d^1(t_{2g})$  transitions of the Eu<sup>2+</sup> ion. A detailed analysis applying the atomic coupling scheme suggests that the peak structures near 1.5 and 2.0 eV may be assigned to the two-photon-resonant spin-allowed and spin-forbidden transition, respectively, from the  $4f^7$  ground state to the  $J$  multiplets in the excited  $4f-5d$  states split by the octahedral crystal field, the exchange coupling, and the spin-orbit interaction.<sup>7,10</sup> In spite of their lower signal yield, nonlinear optical techniques can be a more sensitive probe of the electronic structures and magnetic states than linear optical techniques because of the involvement of multiple light fields. In the present case, the SHG spectra in Fig. 1 reveal rich information including a pronounced polarization dependence and a pronounced peak at the spin-forbidden transition that is not discernible in the weakly structured linear absorption spectrum.<sup>10</sup>

Figure 2(a) shows the temperature dependence of the SHG intensity for  $\chi_{xxy}$  taken at  $2\hbar\omega = 2.60$  eV. The SHG signal disappears exactly at  $T_C$  confirming its purely ferromagnetic origin. Neither crystallographic SHG from the EuO nor SHG from the a-Si and the YAlO<sub>3</sub> substrate contribute to the net signal, which reveals SHG to be a background-free probe of the magnetic state of the EuO in the a-Si/EuO/YAlO<sub>3</sub>

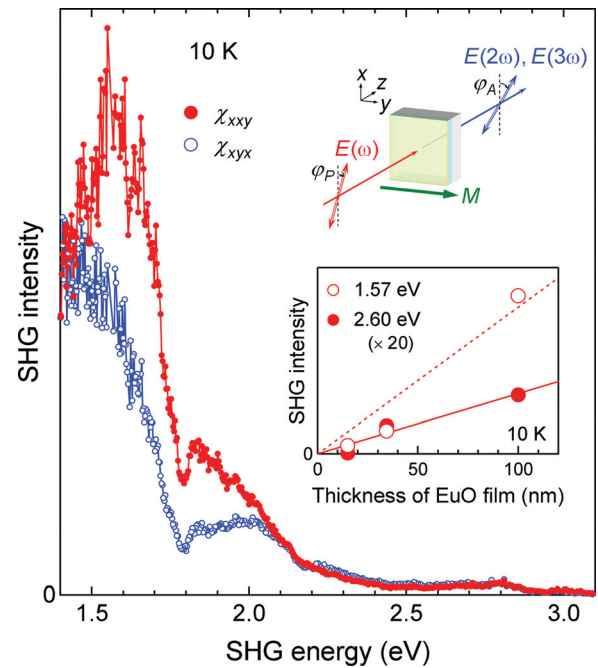


FIG. 1. (Color online) SHG spectra of an epitaxial EuO (001) film at 10 K for  $\chi_{xxy}$  and  $\chi_{xyx}$ . The inset shows thickness dependence of the SHG intensity at 10 K for  $\chi_{xxy}$  at  $2\hbar\omega = 1.57$  and  $2.60$  eV. The experimental configuration of the SHG and THG measurements of a-Si/EuO/YAlO<sub>3</sub> is also sketched.

heterostructure. This contrasts with the work on EuSe and EuTe films grown on BaF<sub>2</sub> substrates where an SHG signal not coupling to the magnetic order was present, presumably because of the (111) orientation of the corresponding films.<sup>14</sup> The inset of Fig. 2(a) shows the magnetic field dependence of the SHG intensity at 10 K. The SHG intensity varies by one order of magnitude with the change of magnetic field. Different minima in field increasing and decreasing runs lead to a butterfly shape that reflects the ferromagnetic hysteresis.<sup>10</sup>

Figure 2(b) shows the temperature dependence of the THG intensity for  $\chi_{xxx}$  taken at  $3\hbar\omega = 2.60$  eV. Although the THG signal is associated with a crystallographic ( $i$ -type) susceptibility, it clearly reveals a sensitivity to the ferromagnetic order emerging at 69 K. To elucidate this unexpected observation, a field-dependent measurement was done at 10 K as shown in the inset of Fig. 2(b). In contrast to the SHG signal, the THG intensity does not depend on the magnetic field. This means that the enhancement of the THG signal below  $T_C$  should be related to a change of magnetic properties not involving linear coupling to the magnetization. Linear coupling would lead to destructive interference

TABLE I. Nonzero time-invariant ( $i$ -type) and time-noninvariant ( $c$ -type) tensor components for bulk MD-SHG and bulk ED-THG in ferromagnetic EuO. The components  $\chi_{ijk}$  and  $\chi_{ijkl}$  were derived by considering  $m3m$  and  $4/mmm$  as crystallographic and magnetic point symmetry, respectively. Only the experimentally relevant components for a spontaneous magnetization parallel to the  $y$  axis and light incident along the  $z$  axis are listed.<sup>15</sup>

	Time-invariant $\chi^{(i)}$	Time-noninvariant $\chi^{(c)}$
Bulk MD-SHG		
$P_i(2\omega) = \epsilon_0(\chi_{ijk}^{(i)} + \chi_{ijk}^{(c)})E_j(\omega)H_k(\omega)$		$\chi_{xxy}, \chi_{xyx}, \chi_{yxx}, \chi_{yyy}$
Bulk ED-THG		
$P_i(3\omega) = \epsilon_0(\chi_{ijkl}^{(i)} + \chi_{ijkl}^{(c)})E_j(\omega)E_k(\omega)E_l(\omega)$	$\chi_{xxx} = \chi_{yyy}, \chi_{xyy} = \chi_{yyx} = \chi_{yxy} = \chi_{xyx} = \chi_{yxx} = \chi_{yyy}$	

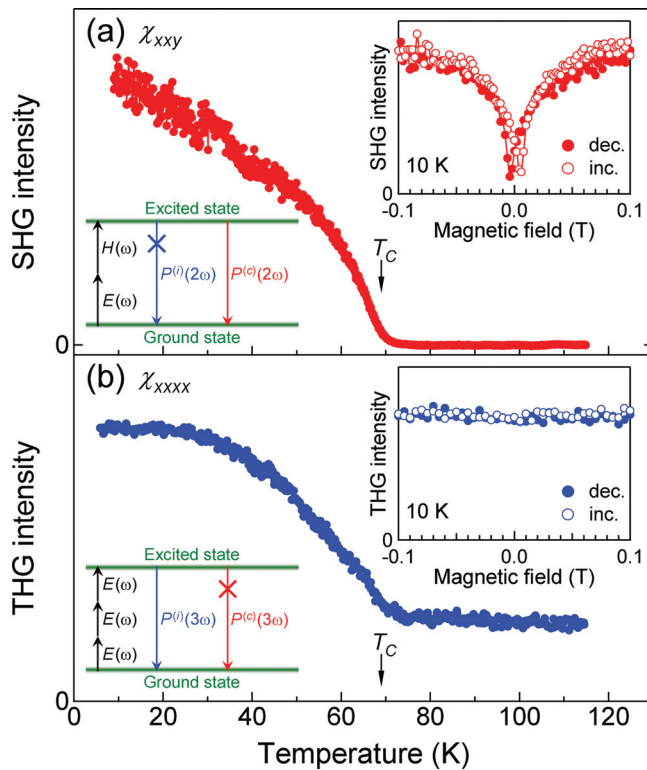


FIG. 2. (Color online) (a) Temperature dependence of SHG intensity from  $\chi_{xy}$  at  $2\hbar\omega = 2.60$  eV. The insets show the magnetic field dependence of the SHG intensity at 10 K and a sketch of the related MD-SHG process. (b) Temperature dependence of THG intensity from  $\chi_{xxx}$  at  $3\hbar\omega = 2.60$  eV. The insets show the magnetic field dependence of the THG intensity at 10 K and a sketch of the related ED-THG process. Data represented by closed (open) symbols in the insets of (a) and (b) were taken with decreasing (increasing) field. Note that *c*-type MD-SHG and *i*-type ED-THG contributions are allowed while *i*-type MD-SHG and *c*-type ED-THG contributions are forbidden by symmetry, as indicated by the crosses.

between the THG contributions from neighboring domains because of the associated  $180^\circ$  phase shift.<sup>11</sup> This would result in a butterfly shape just as in Fig. 2(a). Likewise, a change of linear optical absorption due to temperature-dependent energy shifts of the absorption spectrum<sup>9</sup> cannot explain the observed large enhancement of the THG intensity below  $T_C$  because the change of the linear absorption coefficient with temperature at the photon energies involved in the three-photon excitation is negligible.<sup>10</sup> All of this points to magnetostrictive lattice distortions as the origin of the enhancement of the THG signal. Magnetostriction involves quadratic coupling to the magnetic order and is described by a second-order *i*-tensor.<sup>15</sup> In fact, the temperature behavior of the THG signal in Fig. 2(b) is consistent with that of the earlier observed magnetostriction in EuO,

which reflects the behavior of short-range magnetic order (spin-spin correlation  $\langle \vec{S}_i \cdot \vec{S}_j \rangle$ ).<sup>16</sup> The short-range spin correlation does not change with the magnetic field at low temperature so that the THG signal should not show any field dependence, as observed. Thus, temperature- and field-dependent measurements reveal a linear coupling of the SHG light wave to the magnetization (*c*-type) and a quadratic coupling to the magnetic moments (*i*-type) through magnetostrictive spin-spin correlations as summarized in the sketches in Figs. 2(a) and 2(b).

In summary, MD induced SHG and ED induced THG were observed in the centrosymmetric ferromagnetic semiconductor EuO. The SHG signal shows a linear coupling to the magnetization and detects the long-range ferromagnetic order, while the crystallographic THG signal is largely enhanced by magnetostriction, which is related to short-range spin-spin correlations. These results demonstrate the potential of nonlinear optics for acquiring unique information about the crystallographic, electronic, and magnetic properties of spintronics compounds.

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