Nonlinear Optical Spectroscopy of the Two-Order-Parameter Compound YMnO$_3$

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We have observed two types of optical second harmonic spectra of Mn^{3+} ions in hexagonal YMnO$_3$, one of which is caused by the noncentrosymmetric ferroelectric ordering of charges, whereas the other is due to the centrosymmetric antiferromagnetic ordering of spins. Partial overlapping between the electronic transitions gives rise to a new kind of nonlinear optical polarization $\mathbf{P}(2\omega) = \mathbf{P}^{\mathrm{FE}}(2\omega) + \mathbf{P}^{\mathrm{AFM}}(2\omega)$, which depends on two order parameters. The magnitude and phase of $\mathbf{P}(2\omega)$ can be changed by varying the ratio between the two contributions, as demonstrated by changing the contrast between 180° antiferromagnetic domains, which are indistinguishable in linear optics. [S0031-9007(98)07311-6]

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Physically, the most important part of optical nonlinearity stems from the electric-dipole mechanism, which couples intense electromagnetic laser fields with the positive and negative charges in the medium. The distribution of charges and thus the nonlinear susceptibilities can be changed by an electric field, stress, temperature, etc. Drastic changes of nonlinear susceptibilities occur when the crystal symmetry is broken due to structural phase transitions. In particular, the second-order susceptibility $\chi_{ijk}^{(2)}$, which leads to second harmonic generation (SHG) in noncentrosymmetric media [1], is a linear function of the order parameter (the spontaneous polarization $\mathbf{P}_s$) below the ferroelectric phase transition. The electric-dipole contributions to SHG has been studied in many piezoelectric and ferroelectric crystals and the underlying microscopic mechanisms are well understood.

Recently, a magnetization-induced SHG of electric-dipole character was observed in several magnetic media [2–6]. These experiments have shown that the magnetic contribution to SHG arises at the surfaces, the interfaces, or in the bulk of magnetic materials provided the space-inversion operation is broken. A quite different mechanism of electric-dipole nonlinearity was found in the magnetoelectric crystal Cr$_2$O$_3$ which has a centrosymmetric charge distribution but a noncentrosymmetric antiferromagnetic spin ordering [7]. The contribution to SHG due to the spin ordering was found to be a linear function of the appropriate order parameter [6,7].

In contrast to ferroelectric and magnetic crystals, in which the nonlinear susceptibility is a linear function of only one order parameter, there are materials which may be regarded as media with two order parameters. One is due to the charge ordering and the other is due to the ordering of spins. The coexistence of the two kinds of ordering, having different properties with respect to space inversion and time reversal, may lead to a new type of the nonlinear susceptibility and unusual optical phenomena.

This susceptibility must be a bilinear function of the two order parameters.

In this Letter, we report on the first observation of two types of SH spectra in hexagonal YMnO$_3$, which are due to time-invariant (ferroelectric) and time-noninvariant (antiferromagnetic) susceptibilities. The spectra are attributed to d-d electronic transitions within the Mn^{3+} ions. We show that a new type of the time-noninvariant nonlinear susceptibility may be exhibited by crystals with a *noncentrosymmetric* ordering of charges and a *centrosymmetric* spin ordering. A partial overlapping between the electronic transitions gives rise to a new kind of nonlinear optical polarization which is sensitive to the relative contributions of these two sources. An internal interference may occur opening a possibility of phase-sensitive nonlinear spectroscopy. As an example we show how 180° antiferromagnetic domains, which are indistinguishable in linear optics, become visible in SH light with a high contrast.

The crystallographic, magnetic, and electric properties of hexagonal YMnO$_3$ and other rare-earth manganites were studied in the 1960s and the relevant data can be found in [8]. New data concerning dielectric, magnetic, infrared, and Raman studies have been reported recently [9,10]. Epitaxial films of YMnO$_3$ were recently proposed as new candidates for nonvolatile memory devices [11]. Above the Curie temperature $T_C = 913$ K the crystal structure of YMnO$_3$ is presumably centrosymmetric with the point group $6/mmm$. The Mn^{3+} ions with the electronic structure $(3d)^4$ occupy unusual fivefold coordinated bipyramidal positions with the site symmetry $\bar{6}m2$ [10,12]. Below T_C the YMnO$_3$ structure is described by the point group $6mm$ and the spontaneous ferroelectric polarization $\mathbf{P}_s$ is directed along the sixfold z axis. The Mn^{3+} ions have the site symmetry m. The magnetic properties of YMnO$_3$ arise from the manganese ions Mn^{3+} in the high-spin state, $S = 2$. Below the Néel temperature T_N (according to our

measurements $T_N = 74$ K) the spins of the six Mn^{3+} ions in the unit cell are ordered antiferromagnetically in a triangular structure perpendicular to the polar axis [13]. A strong optical absorption in $YMnO_3$ occurs above 1.28 eV at room temperature and above 1.55 eV at 4 K [14]. This makes the observation of the electronic transitions within the Mn^{3+} ions above these energies difficult by one-photon absorption spectroscopy.

SHG is allowed in $YMnO_3$ in the electric-dipole approximation below T_C due to the ferroelectric (FE) ordering of charges. The relevant polarization $\mathbf{P}^{FE}(2\omega)$ for the point group $6mm$ is given by

$$P_x^{FE}(2\omega) = 2\varepsilon_0 \chi_{xxz}^{(i)} E_x(\omega) E_z(\omega),$$
$$P_y^{FE}(2\omega) = 2\varepsilon_0 \chi_{xxz}^{(i)} E_y(\omega) E_z(\omega), \qquad (1)$$
$$P_z^{FE}(2\omega) = \varepsilon_0 \chi_{zxx}^{(i)} [E_x^2(\omega) + E_y^2(\omega)] + \varepsilon_0 \chi_{zzz}^{(i)} E_z^2(\omega),$$

where the $E_j(\omega)$ ($j = x, y, z$) are the components of the electric field of the fundamental light. Being due to the ordering of charges, the nonlinear susceptibility $\chi_{ijk}^{(i)}$ is of a *time-invariant* type (*i*-type [15]) and a linear function of the ferroelectric order parameter $\mathbf{P}_s$. It contributes to SHG below T_C, and thus also below the antiferromagnetic Néel temperature T_N. Additionally, below T_N a new electric-dipole susceptibility $\chi_{ijk}^{(c)}$ becomes allowed due to the antiferromagnetic ordering of spins. Consequently, this susceptibility is of a *time-noninvariant* type (*c*-type [15]) and a linear function of the antiferromagnetic order parameter. For the magnetic structure $\underline{6}m\underline{m}$ [13], the antiferromagnetic (AFM) contribution $\mathbf{P}^{AFM}(2\omega)$ to the total nonlinear polarization is given by

$$P_x^{AFM}(2\omega) = \varepsilon_0 \chi_{xxx}^{(c)} [E_x^2(\omega) - E_y^2(\omega)],$$
$$P_y^{AFM}(2\omega) = -2\varepsilon_0 \chi_{xxx}^{(c)} E_x(\omega) E_y(\omega), \qquad (2)$$
$$P_z^{AFM}(2\omega) = 0.$$

The polar tensors $\chi_{ijk}^{(i)}$ and $\chi_{ijk}^{(c)}$ in Eqs. (1) and (2) are even and odd functions of the time-reversal operation, respectively. In the region of transparency $\chi_{ijk}^{(i)}$ is real, but $\chi_{ijk}^{(c)}$ is imaginary [16]. In the presence of absorption these susceptibilities are complex.

An unusual character of the nonlinear optical susceptibility $\chi_{ijk}^{(c)}$ in $YMnO_3$ should be emphasized. A time-noninvariant electric-dipole polarization was previously observed either in piezoelectric crystals in the presence of magnetization [2–6] or in magnetoelectric crystals like Cr_2O_3, which possess a centrosymmetric crystal structure and a noncentrosymmetric spin structure [7]. In these cases the magnetic contribution to SHG is a linear function of only one relevant order parameter. The case of $YMnO_3$ is quite different. Below T_N hexagonal $YMnO_3$ belongs to the magnetic point group $\underline{6}m\underline{m}$ where spin ordering is *centrosymmetric* and the space-inversion operation does not change the orientation of spins in the unit

cell [17]. The antiferromagnetic ordering in $YMnO_3$ cannot give rise to $\chi_{ijk}^{(c)}$ in itself, as it occurs in the antiferromagnetic Cr_2O_3, but only due to a coexistence with the ferroelectric ordering. To our knowledge, $\chi_{ijk}^{(c)}$ in $YMnO_3$ is the first example of a nonlinear optical susceptibility which is due to two order parameters. One is due to the spontaneous ferroelectric polarization $\mathbf{P}_s$, whereas the other is due to the centrosymmetric antiferromagnetic ordering of spins.

In the experiments thin (0001) platelets were used, both as-grown and polished, with thicknesses between 0.05–0.1 mm and with lateral dimensions of 1–3 mm. The SH spectra were studied in the range of the pump beam energy $\hbar\omega = 1.0$–1.6 eV at $T = 6$ K, where $YMnO_3$ crystals are transparent. The experimental setup to observe SH spectra was described previously [7]. An optical parametric oscillator pumped by a frequency-tripled Nd:YAG laser was used as a source of the fundamental light. Light pulses of about 2–3 mJ, a pulse width of 5 ns at a repetition rate of 10 Hz were used. SH signals were measured by means of a cooled CCD camera. $YMnO_3$ single crystals are normally unpoled and two types of 180° ferroelectric domains with spontaneous polarization $\mathbf{P}_s$ along the sixfold z axis can be observed using electron microscopy [18]. In our experiments we used unpoled and poled samples. For getting poled samples thin specimens were painted with silver electrodes and a dc electric field of about 60 kV/cm was applied.

The ferroelectric components $\chi_{ijk}^{(i)}$ can be observed only with the polarization of light with only z, or both z and $x(y)$ components. Since all available samples were thin (0001) platelets, the ferroelectric SH spectra could not be observed at normal incidence $\mathbf{k} \parallel z$, but the sample had to be rotated by an angle α around an axis perpendicular to the z axis. Figure 1a shows the ferroelectric SH spectrum at $\alpha = 30°$ (internal angle $= 15°$ due to refraction) with the incoming polarization $\mathbf{E}(\omega) \parallel x$ and the outcoming polarization $\mathbf{E}(2\omega) \perp x$. The spectrum is observed both above and below T_N as a broad band centered at about 2.7 eV. The measurement of the rotational anisotropy was performed for the orthogonal polarizations $\mathbf{E}(\omega) \perp \mathbf{E}(2\omega)$ as a function of the azimuthal angle φ (see inset of Fig. 1a). It shows a twofold symmetry $I(2\omega) \propto (\cos \varphi)^2$ as expected from Eq. (1). When the tilted sample is pumped with linearly polarized light $\mathbf{E}(\omega) \parallel x$ there is a distinct SH signal in the poled area, and only a weak signal in the unpoled area.

The antiferromagnetic SH spectrum due to the $\chi_{xxx}^{(c)}$ component was observed only below T_N at $\mathbf{k} \parallel z$ (see Fig. 1b), where the ferroelectric contributions vanish. It is characterized by a sharper band with a maximum at 2.46 eV. The rotational anisotropy measured for $\mathbf{E}(\omega) \perp \mathbf{E}(2\omega)$ shows a well-defined sixfold pattern (see inset of Fig. 1b). In accordance with the prediction of Eq. (2), the experimental data are well fitted by $I(2\omega) \propto (\chi_{xxx}^{(c)} \sin 3\varphi)^2$, thus allowing a clear distinction
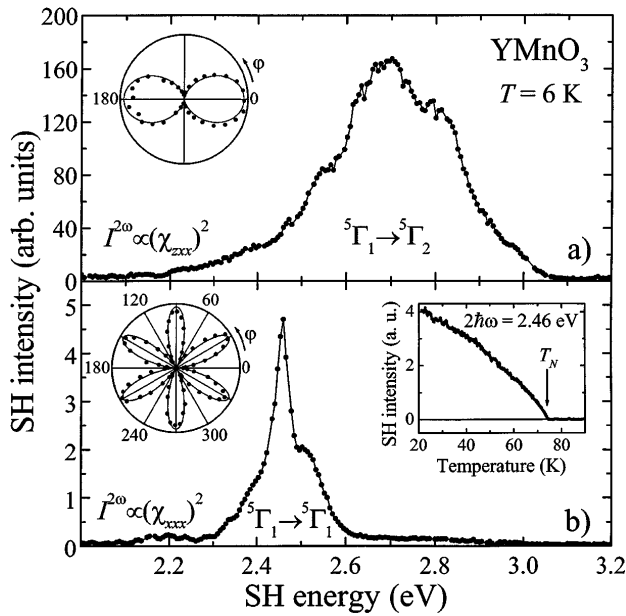
FIG. 1. SHG spectra of YMnO$_3$ due to the ferrelectric ordering (a) and to the antiferromagnetic ordering (b).

FIG. 2. Energy levels of Mn^{3+} ions in the local crystal field of symmetry $\bar{6}m2$ (above T_C) and m (below T_C). The right part of the diagram shows schematically three-photon processes responsible for SHG in YMnO$_3$ below T_N (magnetic symmetry $\underline{6}m\underline{m}$).

between the x and y axes. The calculated curve is shown by the solid line. It is a first observation of such an anisotropy of an antiferromagnetic contribution to SHG. Another inset in Fig. 1b shows the temperature dependence of the antiferromagnetic SH signal taken at $2\hbar\omega = 2.46$ eV. The signal vanishes at T_N and thus confirms directly its relation to the antiferromagnetic order parameter. Such a behavior is in contrast to the measurements of the magnetic susceptibility, which show no anomaly at T_N [9]. The analysis of the temperature dependence of the antiferromagnetic signal below T_N on the basis of the power law $I^{\text{AFM}}(2\omega) \propto (1 - T/T_N)^{2\beta}$ gives directly the critical exponent of the antiferromagnetic order parameter $\beta = 0.38 \pm 0.02$.

The optical spectrum of Mn^{3+} ions in the cubic crystal field of O_h symmetry is due to the spin-allowed transition $^5\Gamma_3(^5E^g) \rightarrow {}^5\Gamma_5(^5T_2^e)$ which usually occurs at 2.5–2.7 eV [19,20]. We are unaware of any report concerning the optical spectra of Mn^{3+} ions in the fivefold coordination. This unusual coordination with the site symmetry $\bar{6}m2$ above T_C leads to a splitting of the $3d$ orbitals into the three sets of $d_{\pm2}, d_{\pm1}, d_0$ orbitals and to a further splitting of these orbitals in the field of symmetry m below T_C [21]. The energy level scheme for the case of localized transitions in the system of four $3d$ electrons is shown in Fig. 2. The ground state is the orbital singlet $^5\Gamma_1(x,y)$, but not the orbital doublet typical for Mn^{3+} ions in the octahedral crystal field [19,20]. The excited states have $^5\Gamma_1(x,y)$ and $^5\Gamma_2(z)$ symmetry. The $^5\Gamma_1 \rightarrow {}^5\Gamma_1$ transition is allowed for $\mathbf{E}(\omega) \perp z$, whereas the $^5\Gamma_1 \rightarrow {}^5\Gamma_2$ transition is allowed for $\mathbf{E}(\omega) \parallel z$. In order to get selection rules for the SHG we have to take into account the crystal symmetry, which averages selection rules over
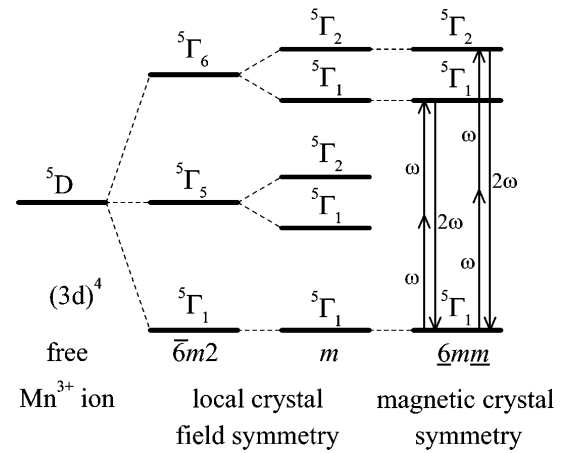
the six Mn^{3+} ions in the unit cell. Averaging leads to a partial overlapping between x, y, and z polarizations due to the fact that the local symmetry axes do not coincide with the crystal symmetry axes. According to Eqs. (1) and (2) we can assign the ferroelectric component observed at $\mathbf{k} \not\parallel z$ to the transition $^5\Gamma_1 \rightarrow {}^5\Gamma_2$ at 2.7 eV and the antiferromagnetic component to the $^5\Gamma_1 \rightarrow {}^5\Gamma_1$ transition at 2.46 eV. The lower energy transition $^5\Gamma_1 \rightarrow {}^5\Gamma_5$ ($^5\Gamma_1, {}^5\Gamma_2$), which is most probably responsible for a strong absorption in YMnO$_3$ above 1.55 eV, has not been studied in the present work.

The time-invariant ferroelectric and the time-noninvariant antiferromagnetic SH spectra overlap in a spectral range from 2.3 to 2.6 eV, thus opening a possibility of a new kind of internal interference between two nonlinear fields of different origin. The interference can be used for visualization of 180° antiferromagnetic domains in the geometry $\mathbf{k} \not\parallel z$ and $\mathbf{E}(\omega) \parallel x$, where the two contributions overlap and thus may interfere. Figure 3 shows the SH contrast between 180° domains at 2.46 eV as a function of the azimuthal angle ϑ of the analyzer. The interference SH spectra were measured separately in two antiferromagnetic domains $+l$ and $-l$ at the analyzer angle $\vartheta = 40°$ with respect to the fixed polarization of the incoming beam $\mathbf{E}(\omega) \parallel x$ (see inset in Fig. 3). The contrast is defined as $\rho = [I(2\omega, +l) - I(2\omega, -l)]/[I(2\omega, +l) + I(2\omega, -l)]$. It can be controlled by changing the position of the analyzer. The data are well fitted by the equation [5]:

$$\rho = 2\Phi \tan\vartheta \cos\delta / [1 + (\Phi \tan\vartheta)^2], \quad (3)$$

where $\Phi = \chi_{zxx}^{(i)} \sin(\alpha/2)/\chi_{xxx}^{(c)} = 2 \pm 0.1$, and $\delta = 40° \pm 2°$ is the phase difference between $\chi_{zxx}^{(i)}$ and $\chi_{xxx}^{(c)}$. Thus, the 180° antiferromagnetic domains indistinguishable in linear optics can be observed by measuring the SHG in a tilted sample. The two domain images depicted
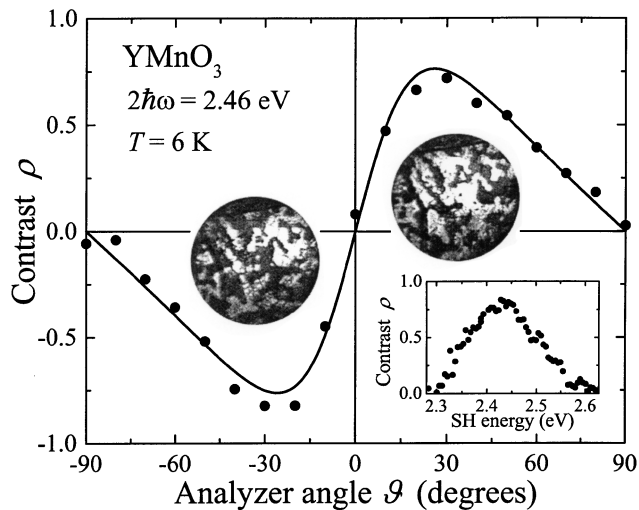
FIG. 3. Change of the contrast between the 180° antiferromagnetic domains as a function of the angle ϑ of the analyzer. The inset shows the contrast as a function of the photon energy in the region where the ferroelectric and antiferromagnetic transitions are overlapping.

in Fig. 3 ($\vartheta = \pm 40°$) show that the contrast is interchanged by changing the analyzer position from negative to positive values. The antiferromagnetic domains are well distinguished in the sample area which is electrically poled. In contrast, SH signals are much weaker in the unpoled area due to the presence of small ferroelectric domains [18], which produce a destructive interference of the SH fields. We suppose that the 180° ferroelectric domains can be visualized using the interference between the ferroelectric SH signal and a SH signal from an external reference [22].

In conclusion, using nonlinear optical spectroscopy we have observed in hexagonal $YMnO_3$ two types of SH spectra, which are unambiguously attributed to the ferroelectric ordering of charges and to the antiferromagnetic ordering of spins, respectively. Both spectra are due to the transitions between the d-d electronic states of Mn^{3+} ions in unusual fivefold coordinated positions. Such an identification of the two sources of nonlinear polarization would be impossible if the study were done at an arbitrary photon energy. Although both contributions are of the electric-dipole character, they possess different properties with respect to the space-time symmetry operations. The assignment of the spectra to the different contributions is supported by a good agreement with a phenomenological model which is based on the crystallographic and magnetic symmetry of $YMnO_3$. The partial overlapping of the two spectra provides the possibility of internal interference between two nonlinear optical fields. The interference conditions can be monitored by varying the amplitude and phase difference between the two nonlinear fields. As an ex-

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