Enhanced Directional Dichroism of Terahertz Light in Resonance with Magnetic Excitations of the Multiferroic $Ba_2CoGe_2O_7$ Oxide Compound

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We propose that concurrently magnetic and ferroelectric, i.e., multiferroic, compounds endowed with electrically active magnetic excitations (electromagnons) provide a key to producing large directional dichroism for long wavelengths of light. By exploiting the control of ferroelectric polarization and magnetization in a multiferroic oxide $Ba_2CoGe_2O_7$, we demonstrate the realization of such a directional light-switch function at terahertz frequencies in resonance with the electromagnon absorption. Our results imply that this hidden potential is present in a broad variety of multiferroics.

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Matter can change color when exposed to a magnetic field. The most exotic manifestation of such magnetochroism is nonreciprocal directional dichroism; that is, materials can distinguish between counterpropagating light beams irrespective of their light polarization. Such a violation of reciprocity can be manifested not only in absorption but also in scattering and refraction processes each governed by the difference in the light velocity (complex index of refraction) for forward and backward propagation [1,2]. The symmetry requirements of directional anisotropy—sharing a common origin with the dc magnetoelectric effect [3]—are rather strict as time reversal and spatial inversion should be simultaneously broken [4,5]. Concerning the microscopic nature of the light-matter interaction, it is closely related to the magnetoelectric linear dichroism, the Jones effect, and the magnetochiral dichroism [2,6–8]. Despite the early prediction of this phenomenon by Brown and co-workers [3], and the efforts donated to its detection with reducing the symmetry of matter, e.g., by application of crossed static electric and magnetic field, the effect was usually found weak from the near infrared to the ultraviolet region of the spectrum [9–11] and also in recent x-ray studies [12]. Directional dichroism has never been evidenced for long wavelengths of light covering the range of magnetic excitations and lattice vibrations in solids. Based on the general concept of multiferroic systems, we show that spin excitations when coupled to electric polarization can be particularly effective to generate directional dichroism controllable by moderate magnetic fields. Furthermore, the effect can be strongly amplified by the spontaneous magnetization and ferroelectric polarization present in multiferroics [13].

In multiferroics, the magnetic and polarization order are coupled to produce the dc magnetoelectric effect; electric polarization can be induced by magnetic field and magnetization appears in response to an electric field [5,14,15]. If the ground state has such an entanglement, the low-lying excitations must also be interlocked. Thus, oscillating magnetization and polarization (M_i^ω and P_i^ω) can be also induced by the electric and magnetic component of light (E_i^ω and H_i^ω), respectively, through the optical magnetoelectric effect (OME) according to $M_i^\omega = 4\pi\chi_{ij}^{me}(\omega)E_j^\omega$ and $P_i^\omega = 4\pi\chi_{ij}^{em}(\omega)H_j^\omega$. Spin and polarization waves can hybridize to form *electromagnons*, as discussed, e.g., in $R\mathrm{MnO_3}$ [16], $R\mathrm{Mn_2O_5}$ [17], and $Ba_2Mg_2Fe_{12}O_{22}$ [18]. A microscopic view based on the Kubo formula shows that resonant electromagnon processes can most efficiently generate the OME:

$$\chi_{ij}^{me}(\omega) = \frac{2}{\hbar}\sum_n \frac{\omega_{no}\Re\{\langle 0|m_i|n\rangle\langle n|e_j|0\rangle\}}{\omega_{no}^2 - \omega^2 - 2i\omega\delta} + \frac{i\omega\Im\{\langle 0|m_i|n\rangle\langle n|e_j|0\rangle\}}{\omega_{no}^2 - \omega^2 - 2i\omega\delta} \quad (1)$$

Dominant contributions arise when transitions from the ground state $|0\rangle$ to excited states $|n\rangle$ can be resonantly induced by photons, i.e. $\omega \approx \omega_{no}$, both via magnetic ($m_i$) and electric ($e_j$) dipole operators. Terms associated with the real($'$) [imaginary($''$)] part of the transition matrix element change sign [remains invariant] under time reversal. The two cross effects are related by the Kubo formula according to $\chi_{ij}^{me}(\omega) = \chi_{ij}'(\omega) + \chi_{ij}''(\omega)$ and $\chi_{ij}^{em}(\omega) = \chi_{ji}'(\omega) - \chi_{ji}''(\omega)$. As also obvious from Eq. (1), the OME changes sign under spatial inversion.

For the study of directional dichroism via the OME of electromagnon excitations, the multiferroic phase of $Ba_2CoGe_2O_7$ offers an ideal arena. A representative part of its tetragonal crystal structure (space group $P\bar{4}2_1m$) is shown in Fig. 1(a). At room temperature it is a paramagnetic insulator with a charge gap of $\Delta \approx 4$ eV. According to preceding studies of neutron scattering [19] and magnetization [20–22], below $T_N = 6.7$ K the spins of Co^{2+} ions lie in the tetragonal plane and form an antiferromagnetic structure with tiny canting along the [110] (or $[1\bar{1}0]$) direction. The onset of the spontaneous magnetization, **M**, is accompanied with a ferroelectric polarization, **P**, pointing along the tetragonal [001] axis [20,21] resulting in a ferrotoroidic state: $\mathbf{T} = \mathbf{P} \times \mathbf{M}$ [5]. The field dependence of the magnetization and the polarization together with the spin texture can be discerned in Figs. 1(b) and 1(c). (Hereafter, the crystallographic axes [110], $[1\bar{1}0]$ and [001] will be referred to as **x**, **y** and **z** direction, respectively.) Though the polarization is an even function of the magnetic field, it can be alternatively reversed either by $\pi/2$ rotation of the field within the xy plane [21] or by π rotation of the sample around the **y** axis, as shown in Fig. 1(d). The feature that **M** and **P** can be separately switched turns out to be a key factor in the control of the directional dichroism.

In the multiferroic phase sketched in Figs. 1(c) and 1(d), the symmetry is lowered to orthorhombic with a magnetic point group of $m_x m'_y 2'_z$ and Neumann's principle yields the following form for the magnetoelectric tensor:

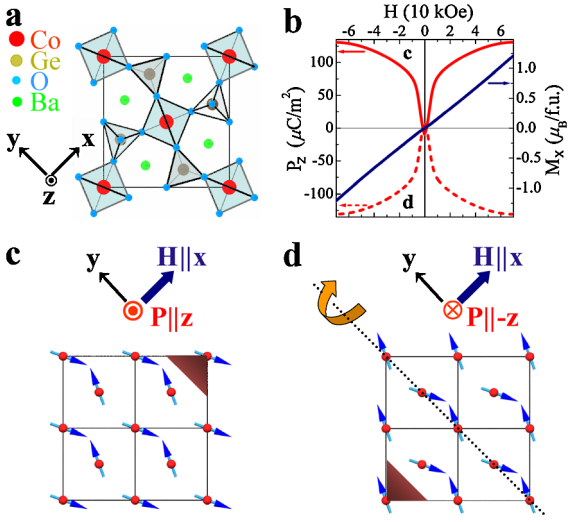

FIG. 1 (color online). (a) Crystal structure of multiferroic $Ba_2CoGe_2O_7$ within layers perpendicular to the tetragonal axis, **z**. Magnetic Co^{2+} ions ($S = 3/2$) form a square lattice. (b) Field dependence of the magnetization (M_x) and the polarization (P_z) at $T = 3.4$ K. Note that the polarization is an even function of H. (c) For $\mathbf{H} \parallel \mathbf{x}$ a single domain with spin structure determined by Ref. [19] is formed and the polarization points to the **z** direction. (d) By π rotation of the crystal around the **y** axis, the polarization is reversed in the frame of the observer while the magnetization is fixed by the external field.

$$\chi_{ij}^{me} = \begin{bmatrix} 0 & \chi''_{xy} & \chi'_{xz} \\ \chi''_{yx} & 0 & 0 \\ \chi'_{zx} & 0 & 0 \end{bmatrix}. \quad (2)$$

Though the same symmetry is possessed by an originally isotropic media after introducing crossed static electric and magnetic field [5,10,14], we will demonstrate that the spontaneous symmetry-breaking fields are far more powerful in producing the OME.

Using terahertz time-domain spectroscopy we have investigated the spin excitations in high-quality single crystals of $Ba_2CoGe_2O_7$ with typical thickness of 1 mm over the frequency range of 0.2–2 THz (0.8–8 meV). (Detailed descriptions of the sample preparation and the applied terahertz method are given in Refs. [21,23], respectively.) Besides the determination of the temperature and field dependence of the transition energies, we have performed a systematic study with change of light polarization, $\mathbf{E}^\omega$ and $\mathbf{H}^\omega$, to establish the selection rules for the different magnon branches. In the multiferroic phase we observed two distinct absorption bands located at ~0.5 THz and ~1 THz in zero field [see Fig. 2(a)]. While the higher-energy mode can be excited for any polarization configuration, the lower one is silent if the magnetic component of the light is parallel to the tetragonal axis, $\mathbf{H}^\omega \parallel \mathbf{z}$. The strength of the 0.5 THz band is independent of the orientation of the light $\mathbf{E}^\omega$ vector implying that this excitation has a dominant magnetic-dipole character. On the other hand, as it is clear from the main polarization configurations shown in Fig. 2(a), the intensity of the sharp transition at ~1 THz changes if either $\mathbf{H}^\omega$ or $\mathbf{E}^\omega$ is varied. Thus, this mode is an *electromagnon* with both electric- and magnetic-dipole activity, and hence should resonantly mediate the OME as expected from Eqs. (1) and (2). From now on, we focus on the configuration of $\mathbf{E}^\omega \parallel \mathbf{P}(\parallel \mathbf{z})$ and $\mathbf{H}^\omega \parallel \mathbf{M}(\parallel \mathbf{x})$, since it turns out to be a unique condition for the directional dichroism phenomenon.

As expected for spin waves, with increasing temperature the absorption of the 0.5 THz mode is gradually reduced and disappears above $T_N \approx 6.7$ K [see Fig. 2(b)]. In contrast, the electromagnon at 1 THz survives above T_N with an increasing redshift and broadening. Both modes show conspicuous magnetochroism; their intensity is enhanced with the application of magnetic field along the **x** direction and a splitting with a g factor ~2 in high fields can be also followed in Fig. 2(c).

We turn to the extraordinary aspect of the electromagnon, namely, its strong directional dichroism. The solution of the Maxwell equations for the symmetry of the multiferroic $Ba_2CoGe_2O_7$ gives clear guidelines. Only when the light propagates perpendicular to both **M** and **P**, i.e. $\mathbf{k} = (0, k_y, 0)$, the directional degeneracy of the optical response is lifted and the velocity becomes different for $\pm k_y$. Consequently, we obtain four independent solutions for the generalized complex refractive index each corresponding to linearly polarized eigenstates:

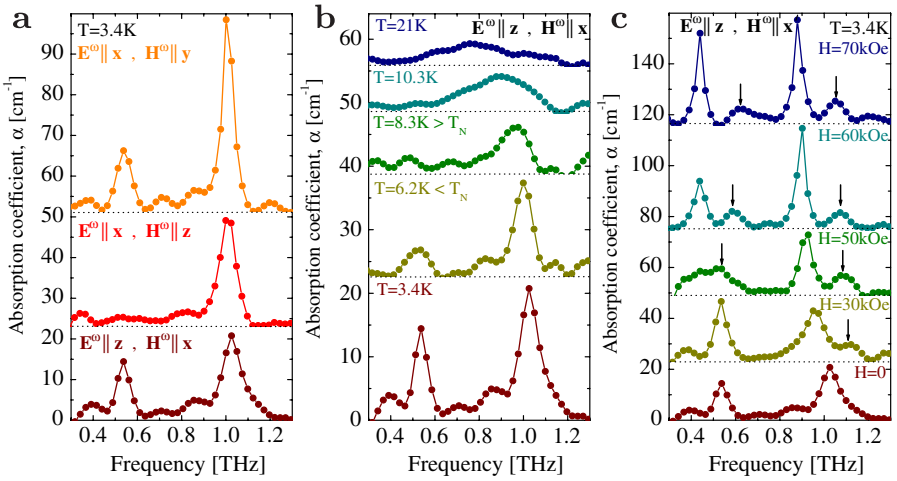

FIG. 2 (color online). Selection rules and characteristics for the magnon modes. The spectra are shifted relative to each other with the corresponding baselines. (a) Light polarization dependence at $T = 3.4$ K in zero field when the **x** and **y** directions are equivalent. The 0.5 THz mode is excited by the $\mathbf{H}^{\omega}$ magnetic component of light but insensitive to the change of the $\mathbf{E}^{\omega}$ electric component. By contrast, the 1 THz mode is clearly affected by the variation of either $\mathbf{H}^{\omega}$ or $\mathbf{E}^{\omega}$. (b) Temperature dependence of the absorption spectrum. The conventional magnon disappears above the Néel temperature, while the electromagnon at 1 THz subsists well above T_N with a considerable fraction of its oscillatory strength present even at ~20 K. (c) At $T = 3.4$ K both modes split into two excitations (the side peaks are indicated by arrows) with the g factor ~2 in high fields.

$$N_{\pm}^{\parallel}(\omega) \approx \pm 4\pi\chi'_{xz}(\omega) + \sqrt{\varepsilon_{zz}(\omega)\mu_{xx}(\omega)}$$
$$N_{\pm}^{\perp}(\omega) \approx \pm 4\pi\chi'_{zx}(\omega) + \sqrt{\varepsilon_{xx}(\omega)\mu_{zz}(\omega)}, \quad (3)$$

where ε_{ij} and μ_{ij} are elements of the electric permittivity and magnetic permeability tensors. $N_{\pm}^{\parallel}$ is the refractive index for $\pm k_y$ in case $\mathbf{E}^{\omega}$ is parallel to the ferroelectric polarization and $\mathbf{H}^{\omega}$ points along the magnetization, while $N_{\pm}^{\perp}$ stands for the perpendicular polarization ($\mathbf{E}^{\omega} \parallel \mathbf{M}$ & $\mathbf{H}^{\omega} \parallel \mathbf{P}$). Then the nonreciprocal term in the complex refractive index, whose real (imaginary) part corresponds to the directional birefringence (dichrosim), is obtained as $\Delta N^{\parallel} = N_{+}^{\parallel} - N_{-}^{\parallel} = 8\pi\chi'_{xz}$ and $\Delta N^{\perp} = 8\pi\chi'_{zx}$. Since ΔN changes sign either by time reversal or spatial inversion, the switching of the magnetization or the polarization of the material is equivalent to the reversal of the light propagation. Therefore, the capability to independently control **M** and **P** is crucial for the rigorous analysis of the optical magnetoelectric phenomena.

Figures 3(a) and 3(b) schematically represent the configuration in which we probed the existence of directional dichroism. We found large nonreciprocal absorption reaching $\Delta\alpha \approx 30$ cm^{-1} in the vicinity of the electromagnon at 1 THz—corresponding in maximum to a relative change of the absorption coefficient $\Delta\alpha/\alpha_{\text{ave}} = 2(\alpha^{+M} - \alpha^{-M})/(\alpha^{+M} + \alpha^{-M}) \approx 0.6$ in $H = \pm 70$ kOe—but no such effect for the magnon mode at 0.5 THz as discerned in Figs. 3(c) and 3(d). Furthermore, $\Delta\alpha$ is reversed when the ferroelectric polarization is "switched" by π rotation of the sample around the **y** axis as shown in Fig. 3(b). Figures 3(c) and 3(d) demonstrate that in easily accessible fields ($H \sim \pm 1$ kOe) the effect remains as high as $\Delta\alpha/\alpha_{\text{ave}} \approx 0.2$. Its further increase with the field strength is in accord with the evolution of the symmetry-breaking order parameters **M** and **P** [see Fig. 3(e)]. While the absorption by the electromagnon mode subsists to some extent above T_N, the temperature dependence of $\Delta\alpha$ in Fig. 3(f) shows that the giant OME is restricted to the multiferroic state.

As argued above, the observation of directional dichroism allows the direct measurement of the magnetoelectric tensor elements, especially those odd in magnetic field. Using the relation between the refractive index and the absorption coefficient, $\Delta\alpha^{\parallel} = 2\omega/c\Im\{\Delta N^{\parallel}\} = 16\pi\omega/c\Im\{\chi'_{xz}\}$, we get $4\pi\Im\{\chi'_{xz}\} \approx 4 \times 10^{-2}$ for the electromagnon at $T = 3.4$ K in $H = 70$ kOe. This number may look small when compared with typical values of the dielectric constant for electric-dipole transitions but it is appreciable on the scale of magnetic-dipole processes. Indeed, for the 0.5 THz magnon excitation—using the background dielectric constant $\varepsilon_{zz} \approx 8$ determined from THz transmission data—we obtain $\Im\{\mu_{xx}\} \approx 1.2 \times 10^{-1}$ under the same conditions. Thus, the OME generating the electromagnon mode at 1 THz is the same order of magnitude as the magnetic susceptibility associated with the pure magnon band. In fact, $\Delta\alpha/\alpha_{\text{ave}}$ found in the order of unity means that the imaginary part of the magnetoelectric susceptibility around $\omega \approx 1$ THz is close to the upper theoretical bound allowed by the second law of thermodynamics according to $\Im\{\sqrt{\varepsilon_{zz}(\omega)\mu_{xx}(\omega)} - 4\pi\chi'_{xz}(\omega)\} \geq 0$. Though the symmetry would also allow directional dichroism for the other polarization when $\mathbf{E}^{\omega} \parallel \mathbf{M}$ & $\mathbf{H}^{\omega} \parallel \mathbf{P}$, we found that $\Delta\alpha^{\perp} \approx 0$ within the precision of the experiment.

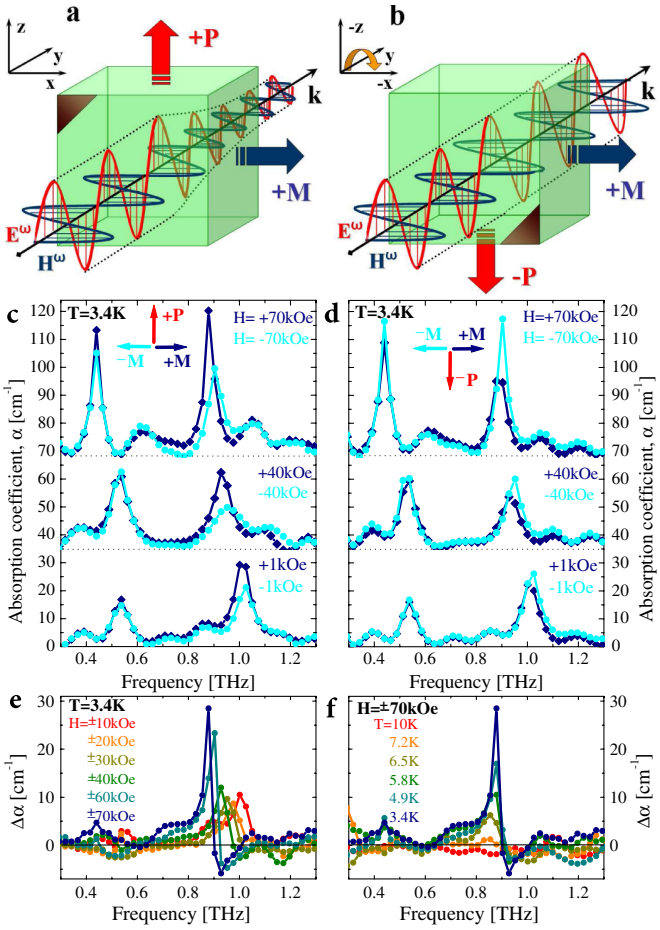

FIG. 3 (color online). Directional dichroism, i.e., the change in the absorption upon reversal of the light propagation, can be equivalently induced by the switching of either the static magnetization (**M**) or the polarization (**P**) of the sample. (a) Because of the resonant absorption, the radiation decays while passing through the material. This loss can be controlled both by **M** ($\parallel \mathbf{H}^{\omega}$) and **P** ($\parallel \mathbf{E}^{\omega}$). (b) For example, the reversal of **P** by π rotation of the sample around the **y** axis can reduce the absorption which is somewhat exaggerated for clarity. (c) and (d) Only the absorption of the electromagnon at 1 THz has a large odd component both in **M** and **P**, and thus shows directional dichroism, $\Delta\alpha$. (e) With an increasing magnetic field $\Delta\alpha$ spectra grow gradually, (f) while it vanishes out of the multiferroic phase above $T_N = 6.7$ K even in $H = 70$ kOe.

Experiments on molecular liquids, which are isotropic in the lack of external fields, imply the same strength for directional dichroism and magnetoelectric linear dichroism [7]. However, the observation of the latter one and its separation from other linear dichroism effects is ambiguous due to the low spatial symmetry of $Ba_2CoGe_2O_7$ and the strong field dependence of the excitations.

In conclusion, we showed that in multiferroic materials the OME can be resonantly enhanced in the range of spin excitations through an electric-dipole–magnetic-dipole interference. Such electromagnon excitations give a unique opportunity to fabricate a magnetically controllable directional light switch for unpolarized microwave and terahertz radiation based on bulk materials. We demonstrated for the case of multiferroic $Ba_2CoGe_2O_7$ that this idea indeed works and a directional dichroism in the order of unity can be realized in the THz region of the electromagnetic spectrum even in weak fields like $H \sim 1$ kOe. Similar functionality is expected to exist in a broad range of multiferroic materials which can potentially nest electromagnons even at room temperature.

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