One-Way Transparency of Light in Multiferroic CuB_2O_4

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We experimentally demonstrate one-way transparency of light in multiferroic CuB_2O_4. The material is rendered transparent for light propagating in one direction, while opaque for light propagating in the opposite direction. The novel transparency results from a destructive interference of the electric dipole and magnetic dipole transitions. The realization of the effect has been accomplished by the application of a high magnetic field and the proper selection of the propagation direction of light in agreement with our quantum mechanical formulation of nonreciprocal directional dichroism.

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When light interacts with matter, an electric (magnetic) field of light produces oscillating electric (magnetic) dipole moments. In multiferroic materials, where the electric dipole moments and the magnetic dipole moments are coupled via the spin-orbit coupling, the oscillating electric (magnetic) dipole moments can be induced also by the magnetic (electric) field of light. In such materials, optical constants may change with the reversal of the propagating direction of light, because the electric and magnetic responses add up with each other for light propagating in one direction, while they cancel out for light propagating in the opposite direction. This phenomenon, which is termed nonreciprocal directional dichroism (NDD), was first experimentally discovered in 1960 for absorption [1] and in 1997 for emission [2]. Recently, the gigantic NDD has been reported in a number of materials [3–15]; however, the NDD has been discussed qualitatively mainly from the point of view of group theory [16]. The quantification of the effect by quantum mechanics may open the way to further enhance the effect.

The NDD is understood in terms of the interference of the electric dipole ($E1$) transition and the magnetic dipole ($M1$) transition in quantum mechanics. According to Fermi's golden rule, the optical absorption coefficients α_+ and α_- for opposite propagation directions are given by

$$\alpha_\pm \propto |\langle e|\mathcal{H}_{E1} \pm \mathcal{H}_{M1}|g\rangle|^2. \quad (1)$$

Here e and g represent the wave function of the excited and the ground states, respectively. $\mathcal{H}_{E1}$ and $\mathcal{H}_{M1}$ are the operators of the electric-dipole and magnetic-dipole transitions, respectively. Usually the optical absorption does not change by the reversal of the propagating direction of light [Fig. 1(a)]. However, Eq. (1) predicts that the interference between the $E1$ and $M1$ transitions results in the NDD [Fig. 1(b)]. In particular, when the $E1$ transition is the same as the $M1$ transition in amplitude, the optical absorption should disappear only for light propagating in one direction. In other words, one-way transparency of light may show up [Fig. 1(c)]. Although the mechanism is quite simple, the experimental realization of the one-way

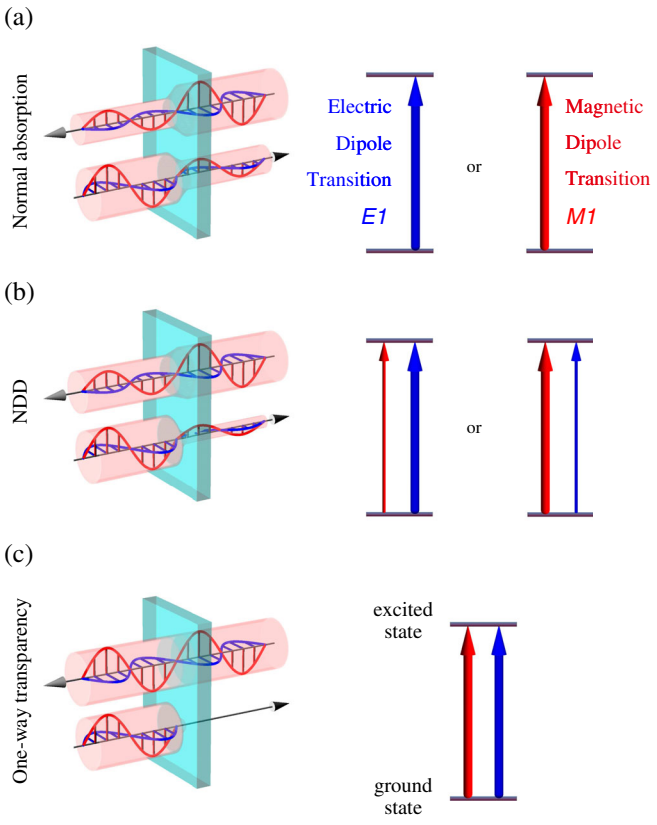

FIG. 1 (color online). Schematic illustration of NDD and one-way transparency of light. (a) Ordinary the optical absorption does not change by the reversal of the propagating direction of light, because it originates from either the $E1$ or $M1$ transition. (b) When the $E1$ and $M1$ transitions interfere with each other, the NDD appears. (c) If the $E1$ transition is equal in amplitude to the $M1$ transition, one-way transparency of light shows up.

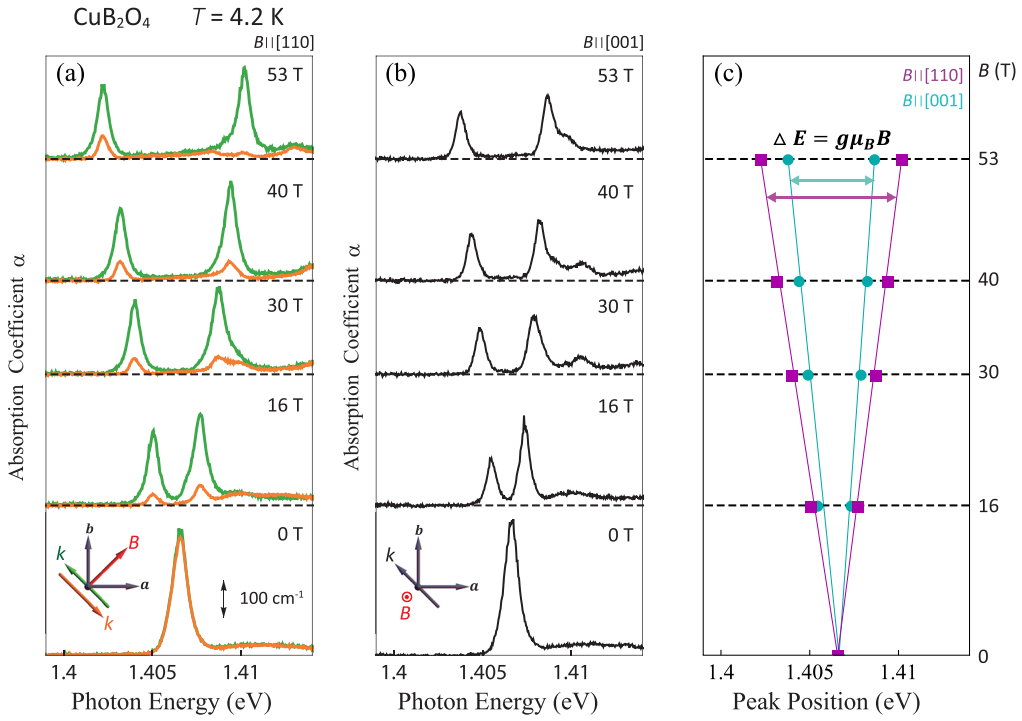

FIG. 2 (color online). Colossal NDD and anisotropic g factor in CuB_2O_4 at 4.2 K. Optical absorption spectra for the linearly polarized light of $E^{\omega}\|[110]$ and $B^{\omega}\|[001]$ in static magnetic fields along (a) the [110] axis and (b) the c axis. Green and yellow lines show the optical absorption spectra for the light propagating in the $[\bar{1}10]$ and the opposite directions, respectively. (c) Magnetic-field dependence of the absorption peak position for the field directions $B\|[110]$ (purple) and $B\|[001]$ (cyan).

transparency of light is a challenge, because the $E1$ transition is usually much stronger than the $M1$ transition for visible and near-infrared lights. In fact, the largest value of the ratio of the optical absorption was $\alpha_+/\alpha_- = 1.001$ in $GaFeO_3$ [17], until it was reported in 2008 that multiferroic CuB_2O_4 shows giant NDD [3–7]. The NDD signal is as large as $\alpha_+/\alpha_- = 3$ for near-infrared light at 1.40 eV. Such a material is a candidate to show the one-way transparency of light.

CuB_2O_4 crystallizes in a noncentrosymmetric tetragonal structure with a space group $I\bar{4}2d$ [18]. Cu^{2+} ions occupy two inequivalent crystallographic sites denoted as A and B. The electronic configuration of the Cu^{2+} site is d^9 (one hole) with $S = \frac{1}{2}$. The giant NDD at 1.40 eV originates from a $d-d$ transition of the Cu^{2+} hole at the A site from the ground state $d_{x^2-y^2}$ to the excited state d_{xy} [3]. Here x, y, and z denote the local coordinate axes at the Cu A site, where z is parallel to the crystallographic c axis. The transition is not only $M1$ allowed but also $E1$ allowed because the excited state d_{xy} is hybridized with d_{yz} and d_{zx} through the spin-orbit coupling. CuB_2O_4 undergoes successive magnetic transitions at $T_N = 21$ and $T^* = 9$ K. Between T_N and T^*, magnetic moments of the Cu^{2+} A site exhibit commensurate easy-plane canted antiferromagnetism, while magnetic moments of the Cu^{2+} B site remain disordered [19–21]. The NDD can be observed only in this phase. Below T^*, magnetic moments at both the A and B sites exhibit incommensurate helical order. At 4.2 K, the helical phase changes to the canted antiferromagnetic phase by applying a magnetic field above the critical field $B_c = 1.2$ T [22]. We expect field-induced NDD above B_c accompanied by the phase transition.

Single crystals of CuB_2O_4 were grown by a flux method [23]. The crystals were oriented using Laue x-ray diffraction patterns, and cut into thin plates of thickness 100 μm. An 18 T magnet at the High Field Laboratory for Superconducting Materials in Tohoku University and a 53 T pulsed magnet at Institute for Solid State Physics in the University of Tokyo were used for the optical measurements in high magnetic fields. The sample was cooled down to liquid helium temperature. The incident light from a halogen lamp was linearly polarized along the [110] axis by using a polarizing film. The intensity spectrum of the transmitted light was measured by using a grating-type optical spectrometer and a CCD detector.

We show in Fig. 2(a) optical absorption spectra in various magnetic fields $B\|[110]$. There are no distinct differences in optical absorption for the light propagating in the $[\bar{1}10]$ (green line) and the opposite directions (yellow line) at 0 T helical phase. We observed NDD induced by a magnetic field above $B_c = 1.2$ T. At higher magnetic fields, the absorption shows the Zeeman splitting. The NDD of the lower-energy peak is weakened with the magnetic field, while it is enhanced for the higher energy peak. The most striking feature is that the higher-energy peak for the light propagating in $[1\bar{1}0]$ direction almost disappears, while it remains for the light propagating in the opposite direction ($[\bar{1}10]$) at $B = 53$ T. The g factor is estimated from the Zeeman splitting energy to be $g^{\mathrm{exp}}_{[110]} = 2.6$ in a magnetic-field $B\|[110]$, suggesting that the orbital contribution to the magnetic moment of the excited state. We show in Fig. 2(b) measurements of the optical absorption in a magnetic field $B\|[001]$, where the estimated g factor is $g^{\mathrm{exp}}_{[001]} = 1.6$. The observed anisotropic g factor

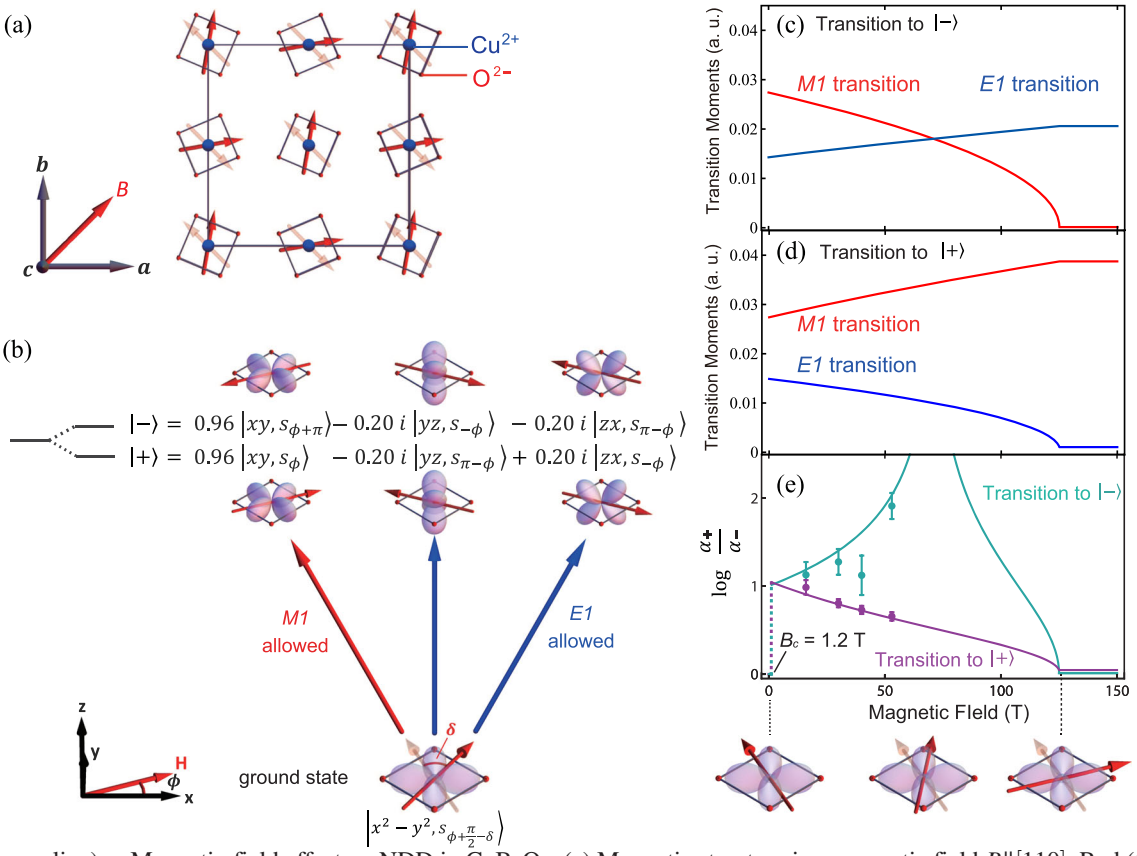

FIG. 3 (color online). Magnetic-field effect on NDD in CuB_2O_4. (a) Magnetic structure in a magnetic field $B\|[110]$. Red (translucent red) arrows show the magnetic moments of Cu^{2+} ions at A site in high magnetic fields (at zero magnetic field). (b) Calculated wave functions of the spin-orbital coupled excited states and the ground state. Transition processes are attached. δ denotes the canting angle of the magnetic moment of the ground state. (c),(d) Magnetic-field dependence of calculated transition dipole moments at (c) the higher energy peak and (d) the lower energy peak. (e) Calculated (solid line) and experimental (dots) values of NDD at the zero-phonon absorption peaks, which are split by Zeeman effect for the light propagating in the $[1\bar{1}0]$ and $[\bar{1}10]$ directions at 4.2 K.

[Fig. 2(c)] suggests that the excited state d_{xy} should be hybridized with other d-orbital states.

We performed a diagonalization calculation considering the crystal-field splitting (d_{xy}:1.40, d_{yz}: 1.67, d_{zx}: 1.67, and d_{z^2}: 1.91 eV) [24,25], the spin-orbit coupling (0.1 eV), and the Zeeman energy with the bases d_{xy}, d_{yz}, d_{zx}, and d_{z^2}. Here we ignored the hybridization between the ground state $d_{x^2-y^2}$ and the excited states because of the large energy gap. The wave functions of the excited states d_{xy} in a magnetic field along $\cos\phi\hat{\mathbf{x}} + \sin\phi\hat{\mathbf{y}}$ are expressed as

$$|+\rangle = A|xy, s_\phi\rangle - Bi|yz, s_{\pi-\phi}\rangle + Ci|zx, s_{-\phi}\rangle, \quad (2)$$

$$|-\rangle = A|xy, s_{\phi+\pi}\rangle - Bi|yz, s_{-\phi}\rangle - Ci|zx, s_{\pi-\phi}\rangle. \quad (3)$$

Here, $|+\rangle$ and $|-\rangle$ are the excited states with the magnetic moment parallel and antiparallel to the magnetic field direction, respectively. $|s_\phi\rangle \equiv (1/\sqrt{2})(e^{-i(\phi/2)}|s_z = +\frac{1}{2}\rangle + e^{+i(\phi/2)}|s_z = -\frac{1}{2}\rangle)$ denotes the spin wave function with the spin moment orienting $\cos\phi\hat{\mathbf{x}} + \sin\phi\hat{\mathbf{y}}$. The obtained coefficients A, B, and C are 0.96, 0.20, and 0.20, respectively. The calculated anisotropic g factors $g^{\mathrm{cal}}_{[110]} = 2.6$ and $g^{\mathrm{cal}}_{[001]} = 1.5$ are in good agreement with the experimental g factors $g^{\mathrm{exp}}_{[110]} = 2.6$ and $g^{\mathrm{exp}}_{[001]} = 1.6$.

In a high magnetic field, the magnetic moments of the ground state are canted toward the magnetic-field direction [26] [Fig. 3(a)], and affect the transition dipole moments. We formulated the NDD by using the wave functions shown in Fig. 3(b) (Supplemental Material [27]). The transition to $|xy\rangle$ is $M1$ allowed with a magnetic field of light along the c axis, while the transitions to $|yz\rangle$ and $|zx\rangle$ are $E1$ allowed with an electric field of light perpendicular to the c-axis. When the magnetic field is strong enough to align the magnetic moments of the ground state to the field direction, the $M1$ transition should become forbidden for the higher-lying energy peak, while the $E1$ transition should remain allowed, because the magnetic moment of the $|xy\rangle$ component in the excited state is antiparallel to the field direction and those of the $|yz\rangle$ and $|zx\rangle$ components are not. In contrast, for the lower-lying energy peak, our quantum mechanical calculation revealed that the $E1$ transition should almost disappear, while the $M1$ transition should remain allowed. We therefore expect that the $M1$ transition should be equal to the $E1$ transition in amplitude

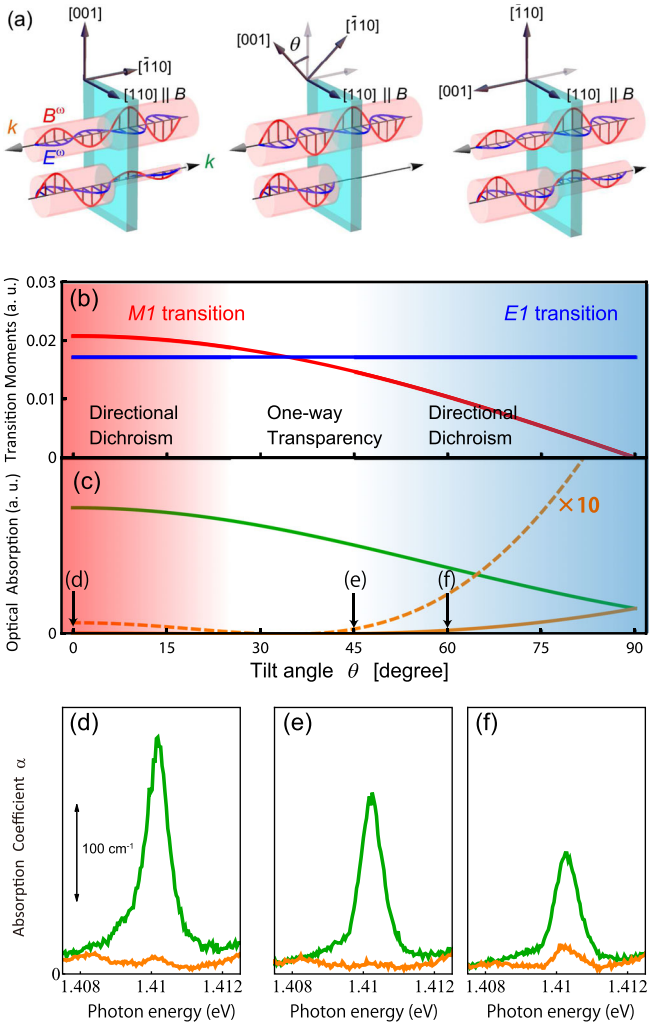

FIG. 4 (color online). One-way transparency of light in CuB_2O_4. (a) Schematic illustration of experimental setups. Optical absorption was measured for several propagation directions of light, which was tilted by an angle θ from $[\bar{1}10]$ to $[00\bar{1}]$. (b) Tilt-angle dependence of the calculated $E1$ (blue) and $M1$ (red) transition dipole moments to the higher-lying energy state at $B = 53$ T. (c) Tilt-angle dependence of the calculated intensity of α_+ (green) and α_- (yellow). (d)–(f) Optical absorption spectra for (d) $\theta = 0°$ (left panel), (e) $\theta = 45°$ (middle panel), and (f) $\theta = 60°$ (right panel) at $T = 4.2$ K in a magnetic field $B = 53$ T along the [110] axis.

for either peak in some magnetic field. We show in Figs. 3(c) and 3(d) calculated magnetic-field dependence of the transition dipole moments for the Zeeman-split doublet. Since the magnetic moments of the $|xy\rangle$ component in the higher (lower)-lying excited state are antiparallel (parallel) to the field direction, the $M1$ transition decreases (increases) in amplitude. On the other hands, the calculation reveals that the $E1$ transition to the higher (lower)-energy peak increases (decreases) with the magnetic field. We show in Fig. 3(e) magnetic-field dependence of the common logarithm of the ratio of the integrated intensity of the optical absorption. The one-way transparency of light ($\alpha_+/\alpha_- = \infty$) is expected at the higher energy lying peak around $B = 75$ T, where the both transitions are predicted to become equal in amplitude.

We realize the one-way transparency of light at 53 T by a trick of the optical alignment. When the sample is rotated around [110] axis [middle panel in Fig. 4(a)], the c component of the magnetic field of light decreases, while the electric field of light keeps parallel to the [110] axis. As a result, the $M1$ transition is weakened, while the amplitude of the $E1$ transition is not affected by the rotation [Fig. 4(b)]. Our calculation predicts that the $M1$ transition should become as small as the $E1$ transition around $\theta = 35°$ at $B = 53$ T, giving rise to the one-way transparency of light [Fig. 4(c)]. Figures 4(d), 4(e), and 4(f) show the optical absorption spectra of the transition to the higher-lying energy state at $B = 53$ T for $\theta = 0°$, $\theta = 45°$, and $\theta = 60°$, respectively. When the B^ω is parallel to the [001] axis ($\theta = 0°$), a weak optical absorption is discernible, since the $M1$ transition is larger than the $E1$ transition. A small optical absorption peak is observed also when $\theta = 60°$, because the $M1$ transition is smaller than the $E1$ transition. By the rotation of the sample to $\theta = 45°$, in contrast, the optical absorption disappears for the light propagating in one direction, while not in the opposite direction, indicating that the $M1$ transition becomes as large as the $E1$ transition.

In conclusion, the one-way transparency of light has been successfully realized in CuB_2O_4 crystal. The perfect cancellation of the electric and magnetic responses of matter to light has an important impact on fundamental physics. The effect may also pave the way to novel optical devices such as optical isolators without using Faraday rotation.

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