Editors' Suggestion

Nonreciprocal Refraction of Light in a Magnetoelectric Material

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In magnetoelectric materials, where the time-reversal and space-inversion symmetries are simultaneously broken, optical properties can differ between the opposite propagation directions of light. We report on an experimental observation of nonreciprocal trajectory of a light ray in magnetoelectric material CuB_2O_4. The light is refracted in different ways between the opposite propagation directions of light. We find a nonreciprocal refraction at the interface between a matter with macroscopic toroidal moment and vacuum. The resultant nonreciprocal deflection of the light is 0.005 deg, which is quantitatively explained using Fermat's principle.

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Magnetoelectrics are materials in which electricity and magnetism are strongly coupled with each other [1]. A distinct feature of these compounds is the magnetoelectric effect——the induction of magnetization (electric polarization) by an electric (magnetic) field. In addition to the static magnetoelectric effect, nontrivial optical phenomena may emerge in magnetoelectric materials because light is a wave of oscillating electric and magnetic fields. A representative example is the nonreciprocity of light propagation—a change in optical properties by the reversal of the propagation direction of light. Such nonreciprocal effects have been reported in a wide frequency range: gigahertz [2,3], terahertz [4–6], near infrared [7,8], visible [9], and x ray [10]. The refractive index n, i.e., the speed of light in ferrotoroidic matter, is expressed as [11]

$$n(\boldsymbol{k}) = n_0 + \frac{\Delta n}{2}\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{T}}. \tag{1}$$

Here Δn denotes the change in refractive index by the reversal of wave vector $\boldsymbol{k}$, and $\boldsymbol{T} \propto \boldsymbol{P} \times \boldsymbol{M}$ is a macroscopic toroidal moment [12], where $\boldsymbol{P}$ and $\boldsymbol{M}$ denote static electric polarization and magnetization in the magnetoelectric material, respectively. $\hat{\boldsymbol{k}}$ and $\hat{\boldsymbol{T}}$ are unit vectors in the direction of $\boldsymbol{k}$ and $\boldsymbol{T}$, respectively. Equation (1) explains that the refractive index changes whether the propagation vector $\boldsymbol{k}$ of light is parallel or antiparallel to the toroidal moment $\boldsymbol{T}$, which is termed nonreciprocal directional birefringence (NDB).

In a conventional birefringent matter like calcite, it is well known that the trajectory of light is different depending on the polarization of light [Fig. 1(a)]. Such a polarization dependent refraction can be explained by Fermat's principle, which states that light takes the path which requires the shortest optical path length, $\int ndr$. Since the refractive index changes with the polarization of light, the trajectory with the minimum optical path length is also polarization dependent. On the other hand, the trajectory of light is unchanged by the reversal of propagation direction of light because the optical path length from point X to point Y, $\int_X^Y n(r)dr$, is always the same as that from Y to X, $\int_Y^X n(r)dr$. However, a remarkable consequence of Eq. (1) is that if the speed of light c/n is direction dependent, the shortest optical path can be different between the opposite propagation directions. Sawada and Nagaosa [11] predicted that light would be deflected in different ways between the opposite propagation directions, when light propagates perpendicularly to rot $\boldsymbol{T}$, which can be nonzero at a 180° toroidal domain wall, for instance. The effect has however not been observed in experiments yet, maybe because detecting the deflection of light at a domain wall is challenging. We experimentally investigate nonreciprocal refraction of light in a single domain ferrotoroidic state, as shown in Fig. 1(b). The refraction of light is expected to be nonreciprocal at the interface between the ferrotoroidic matter and vacuum where rot $\boldsymbol{T}$ has a nonzero value. We have chosen CuB_2O_4 for the investigation since it shows gigantic nonreciprocity for near infrared light at 1.4 eV, which corresponds to a d-d transition of a Cu^{2+} hole [7,8,13–16]. The origin of the nonreciprocity of light is explained by the interference between the electric-dipole and magnetic-dipole transitions mediated by spin-orbit coupling. CuB_2O_4 crystallizes in a noncentrosymmetric tetragonal structure $I\bar{4}2d$ [17]. It shows successive magnetic transitions at 9 and 21 K [18,19]. Between the transition temperatures, the magnetic Cu^{2+} ions at squarely coordinated sites show easy-plane-type canted antiferromagnetic order, while those at distorted octahedral sites remain disordered. We can easily obtain a single magnetic domain state with the application of a magnetic field of about 30 mT. The magnetic point group in a magnetic field along the [110] axis is a polar mm´2´, which allows electric polarization along the c axis [20]. As a consequence, the

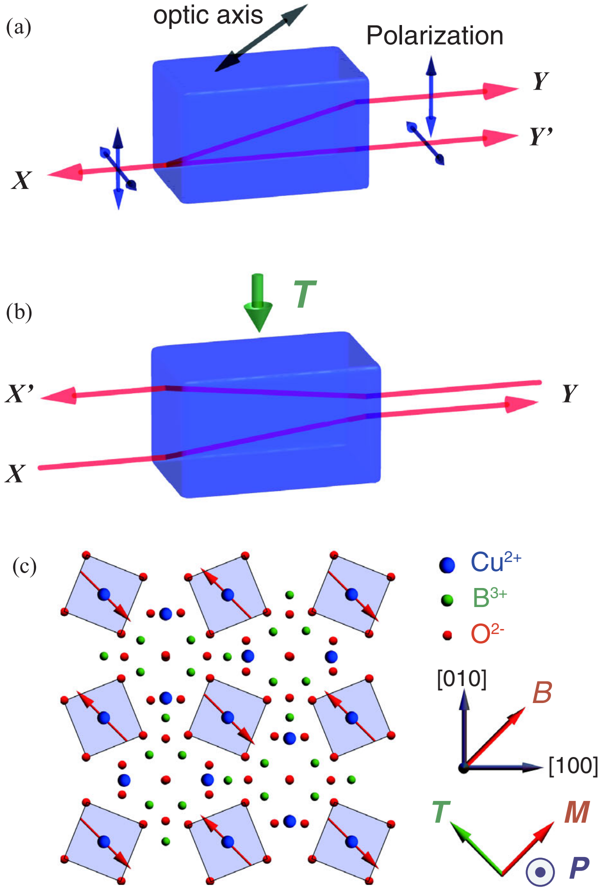


FIG. 1. Schematic illustration of conventional birefringence, nonreciprocal refraction, and the crystal and magnetic structures of $\mathrm{CuB_2O_4}$. (a) In a conventional birefringent matter, a trajectory of light is polarization dependent, and it is reciprocal. When light propagates from a point X to a point Y, it can be sent also from Y to X. (b) In a material with the macroscopic toroidal moment $\boldsymbol{T}$, the reciprocity of the light path breaks down and the trajectory of light can be direction dependent. When light is incident perpendicular to the toroidal moment, the refraction becomes different between opposite propagation directions. Although light propagates from the point X to the point Y, the light from the point Y cannot be sent back to the point X but instead goes to another point, X'. (c) Crystal and magnetic structures of $\mathrm{CuB_2O_4}$ in a magnetic field $B\|[110]$, projected along the tetragonal c axis. Red arrows indicate magnetic moments of the $\mathrm{Cu^{2+}}$ ions at squarely coordinated sites in the canted antiferromagnetic phase. Directions of electric polarization $\boldsymbol{P}$, magnetization $\boldsymbol{M}$, and toroidal moments $\boldsymbol{T}$ are also shown.

toroidal moment $\boldsymbol{T} \propto \boldsymbol{P} \times \boldsymbol{M}$ appears along the $[\bar{1}10]$ axis [Fig. 1(c)], and the optical responses become nonreciprocal for the light propagating along the toroidal moment ($k\|T\|[\bar{1}10]$) [7,8,16]. Notably, the toroidal moment can be reversed by the reversal of the magnetic field since the electric polarization direction is unchanged, while the magnetization is flipped. Therefore, we can detect the nonreciprocal signal by the reversal of the magnetic field instead of a reversal of $\boldsymbol{k}$ [7,16].

Single crystals of $\mathrm{CuB_2O_4}$ were grown by a flux method. Powders of CuO (7.250 g), $\mathrm{B_2O_3}$ (15.228 g), and $\mathrm{LiCO_3}$ (4.041 g) were mixed and put into a Pt crucible. They were heated at 1020 °C in air and then cooled down to 800 °C at a rate of 1.1 °C/h, and to room temperature at a rate of 16 °C/h. The obtained crystal was oriented by using Laue x-ray photographs, then cut into thin plates with the widest faces of (001). The faces were polished to be specularly flat. The thickness of the sample was 3 mm. The sample was mounted on a copper holder with a hole of diameter 300 μm in a He closed-cycled refrigerator. By controlling the temperature of a laser diode, the wavelength of light was tuned to 888 nm, where $\mathrm{CuB_2O_4}$ does not show any optical absorption. The measurement was performed with the application of an ac magnetic field of 50 mT along the [110] axis at a frequency of 1.13 Hz. The beam from the laser diode was passed through the hole of the Cu holder and the sample. The peak position of the transmitted light intensity was measured by a beam profiler (Coherent LaserCam-HR) every 0.2 s.

Figure 2(a) shows an experimental setup for detecting the nonreciprocal refraction, where δ denotes the displacement of the ray of light with the reversal of $\boldsymbol{T}$. Since detecting a change of the beam position with the reversal of $\boldsymbol{k}$ could not be done accurately enough to confirm the nonreciprocity, we measured the displacement of light δ with the reversal of $\boldsymbol{T}$, which can be achieved by the reversal of the external magnetic field. We show in Fig. 2(b) the oscillation of the beam position along the $[\bar{1}10]$ axis of the transmitted light of oscillating electric field $E^{\omega}\|[110]$ and magnetic field $B^{\omega}\|[\bar{1}10]$ in an ac magnetic field at a frequency of 1.13 Hz and an amplitude of $B = 50$ mT along the [110] axis. It is confirmed that the center position of the light ray oscillates along the direction of the toroidal moment about 500 nm at the frequency of the magnetic field. Figure 2(c) shows temperature dependence of the displacement of light δ along the $\boldsymbol{T}$ direction and the magnetization measured in the magnetic field of 50 mT along the [110] axis. Here δ was obtained by the discrete Fourier transformation of the time evolution of the beam center position. The nonreciprocal refraction of light is clearly visible in the canted antiferromagnetic phase where the toroidal moment appears, while it disappears in the helical ($T < 9$ K) and paramagnetic phases ($T > 21$ K). The slight discrepancy of the transition temperatures between the magnetization measurement and the present measurement may come from the low thermal conductivity of $\mathrm{CuB_2O_4}$ and/or thermal contact between the sample and the copper holder. It is of note that the time-reversal symmetry is preserved in the helical and paramagnetic phases. This result indicates that the ferroic toroidal order is essential to the nonreciprocal refraction. Figure 2(d) shows the magnetic-field dependence of the displacement of light at $T = 10$ K. The displacement of light increases with the magnetic field and saturates around $B = 40$ mT, where the

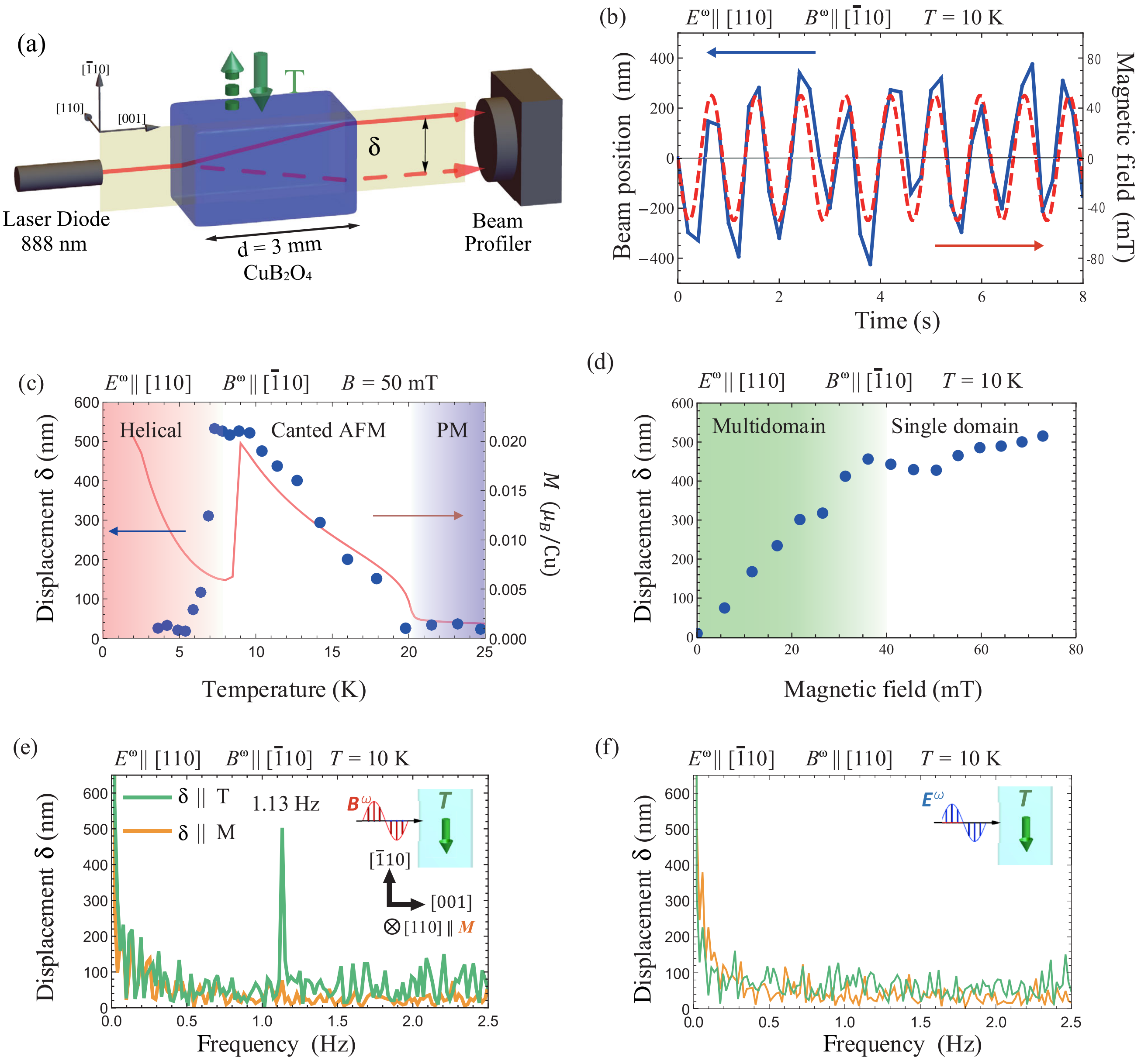
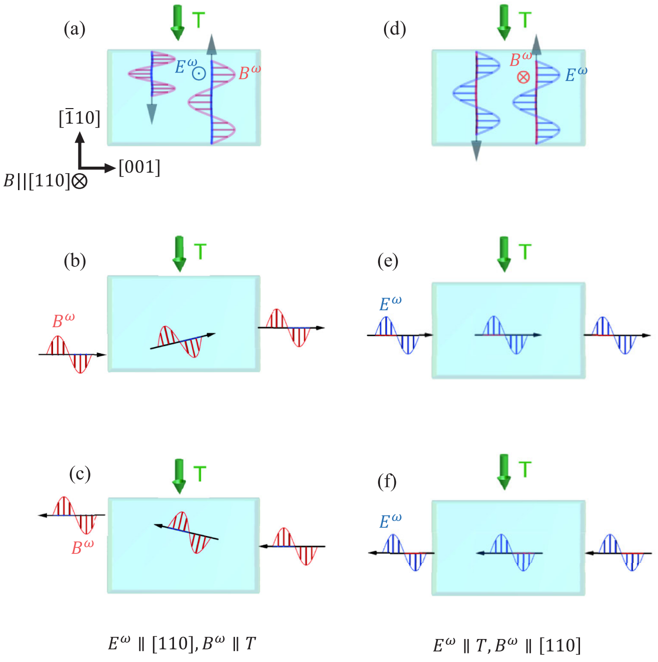


FIG. 2. Experimental observation of nonreciprocal refraction. (a) Experimental setup to detect nonreciprocal refraction. The light with a wavelength at 888 nm was sent from a laser diode to a CuB_2O_4 single crystal. An ac external magnetic field was applied along the [110] axis, and the change in the beam position of the transmitted light with the reversal of the magnetic field was measured by a beam profiler. (b) The detected oscillation of the beam center position of the transmitted light for the linearly polarized light of $E^\omega \| [110]$, $B^\omega \| [\bar{1}10]$. (c) Temperature dependence measured at $B = 50$ mT of magnetization (red) and the displacement of light δ (blue) measured for the linearly polarized light of $E^\omega \| [110]$, $B^\omega \| [\bar{1}10]$. Canted AFM and PM represent the canted antiferromagnetic and paramagnetic phase, respectively. (d) Magnetic-field dependence of δ measured at $T = 10$ K. (e),(f) A discrete Fourier transform of the beam position of light for the linearly polarized light of (e) $E^\omega \| [110]$, $B^\omega \| [\bar{1}10]$ and (f) $E^\omega \| [\bar{1}10]$, $B^\omega \| [110]$. Green and yellow lines show the deflection of light along the toroidal direction $[\bar{1}10]$ and the magnetization direction [110], respectively.

magnetization is aligned to the magnetic-field direction. The displacement of the beam is confirmed to be about 500 nm in the single toroidal domain state.

Next, we discuss the polarization dependence of the effect. Figure 2(e) shows the discrete Fourier transformation of the beam center position in an ac magnetic field of $B = 50$ mT for the linearly polarized light of oscillating electric field $E^\omega \| [110]$ and magnetic field $B^\omega \| [\bar{1}10]$ at $T = 10$ K. Here green and yellow lines show the displacement δ in the $T \| [\bar{1}10]$ and $B \| [110]$ directions, respectively. The light deflects along the toroidal moment at 1.13 Hz, which corresponds to the frequency of the magnetic-field modulation. However, the displacement of light was not observed for the linearly polarized light of



$E^{\omega} \parallel [110], B^{\omega} \parallel T$

$E^{\omega} \parallel T, B^{\omega} \parallel [110]$

FIG. 3. Polarization dependence of the nonreciprocal refraction. (a) Schematic illustration of the nonreciprocal directional birefringence for the linearly polarized light of $E^{\omega}\|[110]$, $B^{\omega}\|[001]$. The speed of light changes whether its propagation direction is parallel or antiparallel to the toroidal moment. (b), (c) Schematic illustration of nonreciprocal propagation of light. When light propagates perpendicularly to the toroidal moment, linearly polarized light of $E^{\omega}\|[110]$, $B^{\omega}\|[\bar{1}10]$ is deflected toward the $-\boldsymbol{T}$ direction because the speed of light becomes faster when the light is deflected toward the $-\boldsymbol{T}$ direction. By the reversal of the propagation direction of light, the light is again deflected toward the $-\boldsymbol{T}$ direction, and the optical path can be nonreciprocal. (d) CuB_2O_4 does not show NDB for the linearly polarized light of $E^{\omega}\|[001]$, $B^{\omega}\|[110]$ because the c component of the magnetic field of light $B^{\omega}\|[001]$ is essential for the nonreciprocity of light. (e) A linearly polarized light along $E^{\omega}\|[\bar{1}10]$, $B^{\omega}\|[110]$ is not deflected since the speed of light does not depend on whether it is deflected toward the $\boldsymbol{T}$ or $-\boldsymbol{T}$ direction. (f) The optical path does not change with the reversal of the propagation direction of light for the polarization of $E^{\omega}\|[\bar{1}10]$, $B^{\omega}\|[110]$.

$E^{\omega}\|[\bar{1}10]B^{\omega}\|[110]$, as shown in Fig. 2(f). The polarization characteristic of the displacement of light can be explained by the selection rules of the d-d transition of the Cu^{2+} hole. The NDB signal originates from the interference between the electric dipole and the magnetic-dipole transitions from the ground state to the excited state at 1.40 eV [8]. The transition is the electric dipole allowed by $E^{\omega}\perp[001]$, while it is the magnetic dipole allowed by $B^{\omega}\|[001]$. When light propagates along the toroidal moment $\boldsymbol{T}$, the NDB shows up for the polarization $B^{\omega}\|[001]$ [Fig. 3(a)], while it does not appear for the polarization $E^{\omega}\|[001]$ [Fig. 3(d)] because $E^{\omega}\perp[001]$ and $B^{\omega}\|[001]$ are essential for the 1.4-eV NDB in CuB_2O_4 [14]. In our experimental setup, the light propagates along the [001] axis, which is perpendicular to the toroidal moment $\boldsymbol{T}$. For the linearly polarized light of $E^{\omega}\|[110]$, $B^{\omega}\|[\bar{1}10]$, a small [001] component of B^{ω} appears when the light deflects along the $\boldsymbol{T}$ direction, as shown in Fig. 3(b). Since the speed of light deflecting to the $-T$ direction is faster than that of it deflecting to the $+T$ direction (NDB), the light should be deflected toward antiparallel to the toroidal moment. When we reverse the propagation direction of light [Fig. 3(c)], the ray of light should bend toward antiparallel to the toroidal moment as well. As a result, the trajectory of light becomes different between the opposite propagation directions. On the other hand, when the electric field of light E^{ω} is parallel to the toroidal moment [Fig. 3(e)], the [001] component of B^{ω} is absent even if the light deflects along the $\boldsymbol{T}$ direction because B^{ω} keeps parallel to the [110] axis. The light should not bend because the speed of light depends little on whether the propagation direction of light is parallel or antiparallel to the toroidal moment, as shown in Fig. 3(d). The optical path does not change by the reversal of the propagation direction for $E^{\omega}\|T$ [Figs. 3(e) and 3(f)].

Although the observed oscillation of light may originate from the nonreciprocal refraction, one should also consider other possible effects which can produce the oscillation of the beam, such as the Cotton-Mouton effect, magnetic noise, and the oscillation of the sample due to the magnetic force. The nonreciprocal refraction should be distinguished from these effects. If the signal would originate from the Cotton-Mouton effect, the frequency of the displacement of light should be observed at 2.26 Hz because the Cotton-Mouton effect is proportional to the square of the magnetization strength M^2. Other possibilities such as magnetic noise and sample oscillation should not contribute to the detected signal because the displacement of light disappears when the polarization of light is $E^{\omega}\|[\bar{1}10]B^{\omega}\|[110]$. We hence conclude that the detected shift of light should originate from the nonreciprocal refraction of light.

Let us quantitatively estimate the shift of the light path by using Fermat's principle. By using the deflection angle θ (Fig. 4), the displacement of light can be expressed as

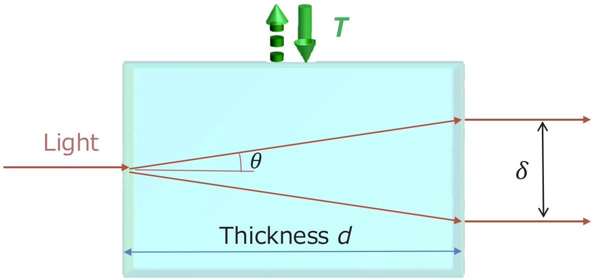


FIG. 4. Schematic illustration of the displacement of light δ due to the reversal of the toroidal moment. The blue box indicates the sample. The green arrows indicate the toroidal moments. θ and d denote the deflection angle of light and the thickness of the sample, respectively.

$\delta = 2d\sin\theta$, where $d = 3$ mm denotes the thickness of the sample. The optical path length $s(\theta)$ in the sample is represented as

$$s(\theta) = \int n(\theta) dr = \left(n_0 - \frac{\Delta n}{2}\theta\right) d \left(1 + \frac{\theta^2}{2}\right).$$

By differentiating $s(\theta)$ with respect to θ, the minimum condition for the optical path length $\theta = \Delta n / 2n_0$ can be obtained. According to the measurement of the nonreciprocal directional birefringence, the change Δn in the refractive index between the opposite propagation directions of light is $\Delta n \sim 3 \times 10^{-4}$ at 888 nm [14]. The displacement δ is given by

$$\delta = 2d\sin\theta \sim \frac{1000}{n_0}\ \text{nm},$$

which is in a good agreement with the experimental value $\delta = 500$ nm.

In summary, we experimentally investigated a nonreciprocal refraction phenomenon originating from NDB in the single toroidal domain state CuB_2O_4. The nonreciprocal refraction was confirmed in the canted antiferromagnetic phase. The displacement δ of the light ray was quantitatively explained by Fermat's principle. While it is usually assumed that the optical path would not change with the reversal of the propagation direction of light, this Letter shows that this is not always correct in magnetoelectric materials. Although the magnitude of the effect, 500 nm, is small, the nonreciprocal refraction is observable in a magnetoelectric material. Large nonreciprocal refraction may be found in terahertz region, where the gigantic NDB signals of $\Delta n \sim 0.6$ were reported [5,6]. In addition, the NDB signal can be dramatically enhanced by fabricating photonic crystals [21,22], which may lead to the gigantic nonreciprocal refraction.

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[1] M. Fiebig J. Phys. D **38**, R123 (2005).
[2] Y. Nii, R. Sasaki, Y. Iguchi, and Y. Onose, J. Phys. Soc. Jpn. **86**, 024707 (2017).
[3] Y. Okamura, F. Kagawa, S. Seki, M. Kubota, M. Kawasaki, and Y. Tokura, Phys. Rev. Lett. **114**, 197202 (2015).
[4] I. Kézsmárki, N. Kida, H. Murakawa, S. Bordács, Y. Onose, and Y. Tokura, Phys. Rev. Lett. **106**, 057403 (2011).
[5] Y. Takahashi, Y. Yamasaki, and Y. Tokura, Phys. Rev. Lett. **111**, 037204 (2013).
[6] A. M. Kuzmenko, V. Dziom, A. Shuvaev, A. Pimenov, M. Schiebl, A. A. Mukhin, V. Y. Ivanov, I. A. Gudim, L. N. Bezmaternykh, and A. Pimenov, Phys. Rev. B **92**, 184409 (2015).
[7] M. Saito, K. Taniguchi, and T. H. Arima, J. Phys. Soc. Jpn. **77**, 013705 (2008).
[8] S. Toyoda, N. Abe, S. Kimura, Y. H. Matsuda, T. Nomura, A. Ikeda, S. Takeyama, and T. Arima, Phys. Rev. Lett. **115**, 267207 (2015).
[9] J. H. Jung, M. Matsubara, T. Arima, J. P. He, Y. Kaneko, and Y. Tokura, Phys. Rev. Lett. **93**, 037403 (2004).
[10] M. Kubota, T. Arima, Y. Kaneko, J. P. He, X. Z. Yu, and Y. Tokura, Phys. Rev. Lett. **92**, 137401 (2004).
[11] K. Sawada and N. Nagaosa, Phys. Rev. Lett. **95**, 237402 (2005).
[12] N. A. Spaldin, M. Fiebig, and M. Mostovoy, J. Phys. Condens. Matter **20**, 434203 (2008).
[13] M. Saito, K. Ishikawa, K. Taniguchi, and T. Arima, Phys. Rev. Lett. **101**, 117402 (2008).
[14] M. Saito, K. Ishikawa, K. Taniguchi, and T. Arima, Appl. Phys. Express **1**, 121302 (2008).
[15] M. Saito, K. Ishikawa, S. Konno, K. Taniguchi, and T. Arima, Nat. Mater. **8**, 634 (2009).
[16] S. Toyoda, N. Abe, and T. Arima, Phys. Rev. B **93**, 201109(R) (2016).
[17] M. Martinez-Ripoll, S. Martínez-Carrera, and S. García-Blanco, Acta Crystallogr. Sect. B **27**, 677 (1971).
[18] G. Petrakovskii, D. Velikanov, A. Vorotinov, A. Balaev, K. Sablina, A. Amato, B. Roessli, J. Schefer, and U. Staub, J. Magn. Magn. Mater. **205**, 105 (1999).
[19] R. V. Pisarev, I. Sänger, G. A. Petrakovskii, and M. Fiebig, Phys. Rev. Lett. **93**, 037204 (2004).
[20] N. D. Khanh, N. Abe, K. Kubo, M. Akaki, M. Tokunaga, T. Sasaki, and T. Arima, Phys. Rev. B **87**, 184416 (2013).
[21] K. Sawada and N. Nagaosa, Appl. Phys. Lett. **87**, 042503 (2005).
[22] N. Kida, Y. Kaneko, J. P. He, M. Matsubara, H. Sato, T. Arima, H. Akoh, and Y. Tokura, Phys. Rev. Lett. **96**, 167202 (2006).