PHYSICAL REVIEW B **96**, 121102(R) (2017)

Magneto-chiral dichroism of $CsCuCl_3$

N. Nakagawa,[1] N. Abe,[1] S. Toyoda,[1] S. Kimura,[2] J. Zaccaro,[3,4] I. Gautier-Luneau,[3,4] D. Luneau,[5] Y. Kousaka,[6,7] A. Sera,[8] M. Sera,[9] K. Inoue,[7,8] J. Akimitsu,[6,7] Y. Tokunaga,[1] and T. Arima[1]

[1]*Department of Advanced Materials Science, University of Tokyo, Kashiwa 277-8561, Japan*
[2]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*
[3]*University Grenoble Alpes, Institut NÉEL, F-38042 Grenoble, France*
[4]*CNRS, Institut NÉEL, F-38042 Grenoble, France*
[5]*Université de Lyon, Université Claude Bernard Lyon 1, Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615, F-69622 Villeurbanne, France*
[6]*Research Institute for Interdisciplinary Science, Okayama University, Okayama 700-8530, Japan*
[7]*Center for Chiral Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*
[8]*Graduate School of Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*
[9]*Department of ADSM, Hiroshima University, Higashi-Hiroshima 739-8530, Japan*

(Received 8 May 2017; published 1 September 2017)

In this Rapid Communication, we investigate the magneto-chiral dichroism (MChD) of right- and left-handed $CsCuCl_3$ crystals in a strong magnetic field up to 14.5 T. We perform near-infrared optical measurements, and the results show a change in the absorption coefficient of an intra-atomic d-d transition in a Cu^{2+} ion at approximately 1.5 eV. The magnitude of MChD was found to be proportional to the magnetization, which depends on the magnetic field and temperature. We verify this relation by developing a simple $CuCl_6$ cluster model.

DOI: 10.1103/PhysRevB.96.121102

Symmetry breaking in materials is essential to optical phenomena. Space-inversion symmetry breaking in chiral media causes natural circular dichroism (NCD). When the time-reversal symmetry is broken by a magnetic field or magnetization, magnetic circular dichroism (MCD) occurs. Further, if the space inversion and time reversal are simultaneously broken, nonreciprocal directional dichroism (NDD) may appear. NDD is the variation in the optical absorption that results from the reversal of the optical propagation direction. NDD in a polar magnet is often referred to as an optical magnetoelectric (OME) effect, while that in chiral media is known as magneto-chiral dichroism (MChD). It has been proposed that MChD originates from the correlation of NCD and MCD [1]. The dielectric functions ε_+ for right-handed circularly polarized light and ε_- for left-handed circularly polarized light are respectively expressed by a function of the z component (z is the direction of light propagation) of the magnetization vector M_z and the propagation vector k_z as

$$\varepsilon_\pm = \varepsilon_0 \pm \alpha_{\mathrm{NCD}} k_z \pm \beta_{\mathrm{MCD}} M_z + \gamma_{\mathrm{MChD}} k_z M_z. \quad (1)$$

The first experimental observation of MChD was reported by Rikken and Raupach [2]. They also observed chirality-dependent photochemistry with unpolarized light in a magnetic field [3]. Although MChD has been observed for several materials in various frequency ranges [4–12], few studies have investigated its quantitative temperature and magnetic-field dependence [10–12]. Therefore, it would be of great significance to conduct a detailed survey on the magnetic-field and temperature dependence of MChD in order to verify whether MChD is proportional to magnetization.

In this Rapid Communication, we focus on the chiral antiferromagnetic material $CsCuCl_3$. $CsCuCl_3$ undergoes a structural phase transition at $T_c = 423$ K and a magnetic phase transition at $T_N = 10.5$ K [13,14]. The space group of $CsCuCl_3$ above 423 K is centrosymmetric $P6_3/mmc$. Below T_c, the cooperative Jahn-Teller effect of Cu^{2+} induces a distortion in $CuCl_6$ octahedra. The crystalline structure changes into a chiral structure with space group $P6_122$ (right handed) or $P6_522$ (left handed) [13]. The structure of right-handed $CsCuCl_3$ is shown in Fig. 1(a). $CuCl_6$ octahedra are connected by sharing a face to form chains along the c axis. The elongated bond direction is shifted by 60° between adjacent $CuCl_6$ octahedra, resulting in the chiral structure. Below 10.5 K, Cu^{2+} spins ($S = \frac{1}{2}$) form a helical magnetic structure of a screw axis parallel to the c axis [14], while a 120° spin structure is formed in each triangular lattice in the ab plane. If a magnetic field is applied along the c axis, the magnetization increases slightly at $H_T = 12$ T and is saturated around 30 T [15,16]. This jump is caused by a metamagnetic transition from an umbrella spin structure to a two-up-one-down coplanar one. This metamagnetic transition is theoretically explained by considering quantum fluctuation [17–19]. Despite the long history of studying $CsCuCl_3$ [13–22], to date, the MChD of $CsCuCl_3$ has not yet been reported due to the difficulty of growing a large homochiral crystal. The typical enantiopure (composed of only left- or right-handed crystals) domain size in a racemic (containing both left- and right-handed crystals) twinned crystal is 10 μm order [23].

Enantiopure right-handed and left-handed $CsCuCl_3$ crystals were grown in solutions of CsCl and $CuCl_2$ either by lowering the temperature in a HCl aqueous solution or by the slow evaporation of slightly acidified water [24]. Crystal orientations were determined by x-ray Laue photographs. Crystals were cut perpendicular to the c axis and ground into thin plates. The thicknesses of the samples were 60 μm ($P6_122$) and 80 μm ($P6_522$). Figure 1(b) shows the experimental setup of the optical absorption measurement in a magnetic field. The $CsCuCl_3$ sample was put on a glass stage with a metal foil mask that had a hole of the order of 1 mm^2. These samples

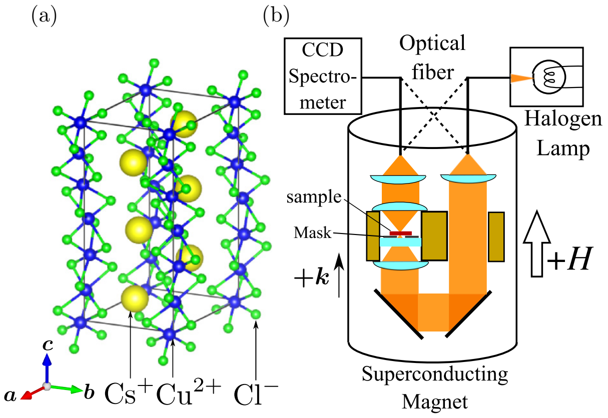

FIG. 1. (a) Crystalline structure of right-handed (space group $P6_122$) $CsCuCl_3$. Cu^{2+} helical chains run along the c axis. This figure was produced using VESTA [25]. (b) Schematic of the measurement system. The directions of $\boldsymbol{H}$ and $\boldsymbol{k}$ are defined as shown. The direction of light was reversed by changing the fibers, as shown by the dotted lines.

were placed in a cryostat equipped with a superconducting magnet. Then, unpolarized light from a halogen lamp was focused on the sample, and the transmitted light intensity was measured by a spectrometer equipped with a CCD detector. The propagation direction of light was switched between $+c$ and $-c$ by exchanging the optical fibers. The magnetic field was applied parallel or antiparallel to the propagation vector of light. The MChD spectrum was derived by calculating the differential absorption coefficient with the reversal of $\boldsymbol{k}$ or $\boldsymbol{H}$.

The obtained spectra of MChD around 1.5 eV are shown in Figs. 2(a) and 2(b). The sign of the MChD effect is dependent on the magnetic-field direction and the crystal chirality. This behavior is entirely consistent with the characteristics of MChD, as shown in Eq. (1). The shapes of MChD spectra for $P6_122$ and $P6_522$ are slightly different from one another, and this may be because of factors such as the inhomogeneous thicknesses. Figure 2(c) shows the spectrum of the absorption coefficient α at zero magnetic field. The magnitude of MChD $\Delta\alpha/\alpha$ at 1.5 eV is 0.3% per 1 T. Figure 2(d) shows the magnetic-field dependence of MChD at 1.5 eV. The MChD signal is proportional to the magnetic field at 15 K (blue circles). In contrast, a small step can be observed between 12 and 13 T at 4.2 K (red circles). It is noteworthy that $CsCuCl_3$ undergoes a metamagnetic transition at around 12 T, as shown by the solid line. The similar magnetic-field dependence implies that MChD should be proportional to the magnetization. The magnetic-field dependence of MChD in $P6_522$ crystal is shown in the Supplemental Material [26].

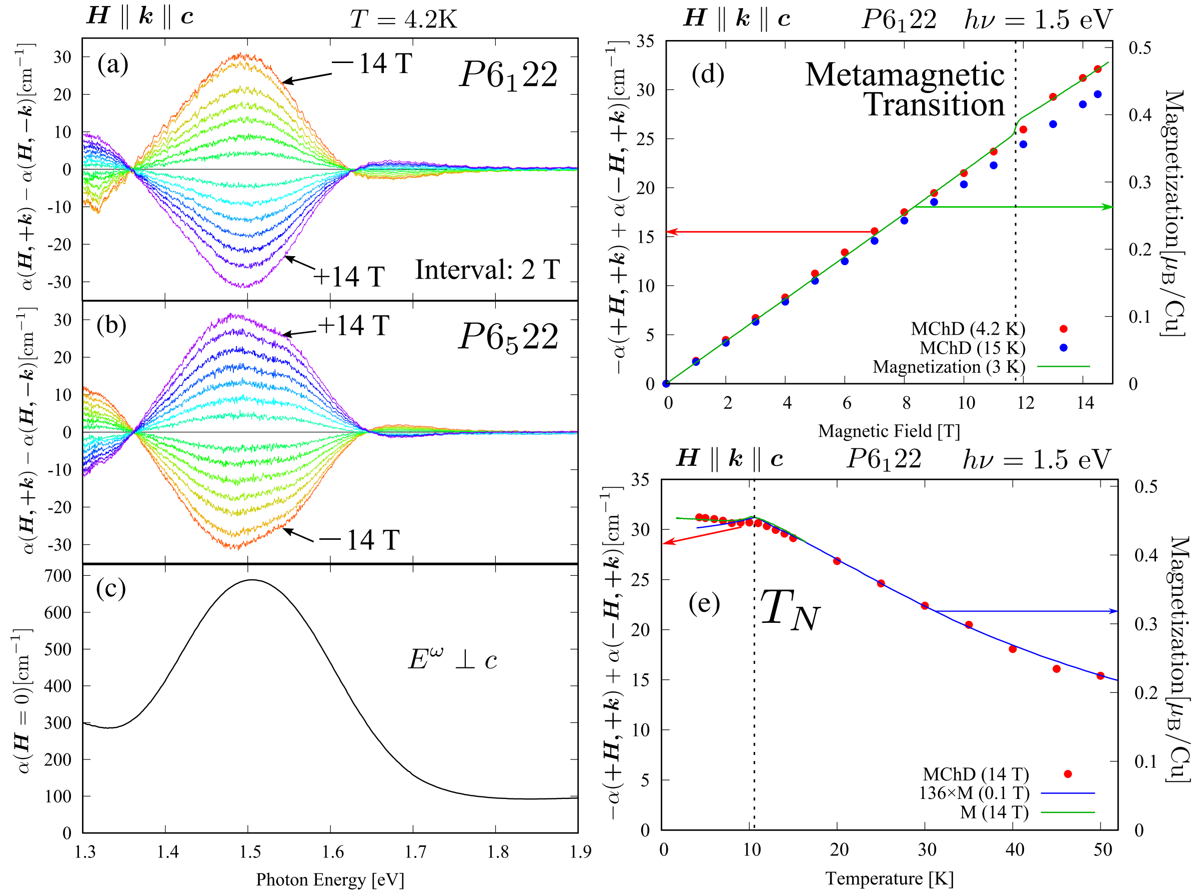

FIG. 2. H-odd component of absorption coefficient change, which is attributed to the magneto-chiral dichroism. (a), (b) Magnetic-field dependence of MChD spectrum, in (a) right-handed and (b) left-handed $CsCuCl_3$ at 4.2 K. (c) Absorption spectrum of $CsCuCl_3$ at 4.2 K. (d) Magnetic-field dependence of MChD at 1.5 eV and magnetization of $CsCuCl_3$ at 3 K [17]. (e) Temperature dependence of MChD at 1.5 eV and magnetization of $CsCuCl_3$ at 14 T [17] (green line). The blue line shows M at 0.1 T.

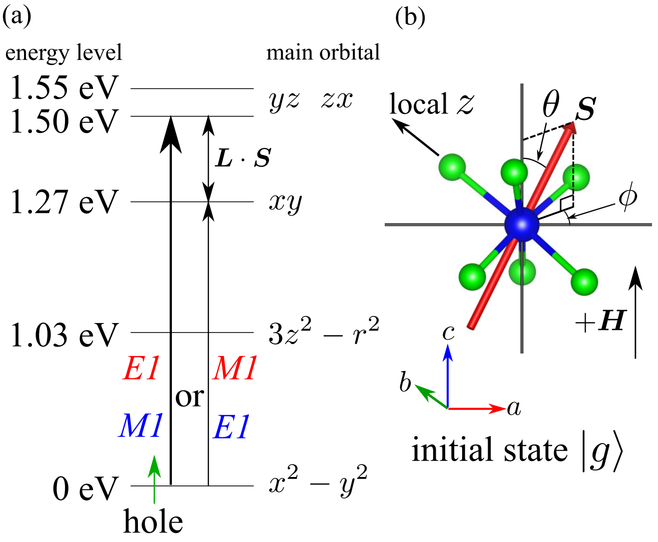

FIG. 3. (a) Energy levels of d orbitals of Cu^{2+} ion in $CsCuCl_3$. These energies are determined by a Gaussian fitting of the optical absorption spectrum. (b) Spin configuration of the initial state.

Figure 2(e) shows the temperature dependence of MChD at around 1.5 eV and the M-T curve at 14 T. The MChD curve at around 10 K shows a cusp at T_N. The peak magnitude of MChD is larger than in other reported paramagnetic media in the near-infrared region [6,7]. The value of MChD above T_N fits the M-T curve at a weak magnetic field of 0.1 T (blue line). We conclude that MChD should be scaled to the magnetization in the paramagnetic state.

Nonreciprocal directional dichroism including MChD is generally understood as an interference between electric dipole ($E1$) and magnetic dipole ($M1$) transitions resulting from spin-orbit coupling ($\lambda\boldsymbol{L}\cdot\boldsymbol{S}$) [27–29]. Figure 3(a) shows the energy diagram of Cu^{2+} $3d$ orbitals in an elongated $CuCl_6$ octahedron in the hole picture [30]. The wave function of the initial state $|g\rangle$ is expressed as

$$|g\rangle = \cos\frac{\theta}{2}e^{-i\frac{\phi}{2}}|s_\uparrow\rangle + \sin\frac{\theta}{2}e^{i\frac{\phi}{2}}|s_\downarrow\rangle. \qquad (2)$$

Here, $|s_\uparrow\rangle$ ($|s_\downarrow\rangle$) is the wave function of the spin (anti)parallel to the c axis. The spin is oriented in the direction defined by angles θ and ϕ [see Fig. 3(b)]. The macroscopic magnetization $\boldsymbol{M}(\parallel c)$ is calculated as $\boldsymbol{M} = Ng\mu_B\langle\cos\theta\rangle/2$, where N is the density of Cu^{2+} spins, g is the g-factor, and μ_B is a Bohr magneton.

Let us consider the excited states $|e_\uparrow\rangle$ and $|e_\downarrow\rangle$. If the effective magnetic field is zero, these states would be at the same energy level as those by Kramers degeneracy. The magnitude of MChD $\Delta\alpha_\uparrow$ for the transition to $|e_\uparrow\rangle$ is calculated as

$$\begin{aligned}\Delta\alpha_\uparrow &\propto |\langle e_\uparrow|\mathcal{H}_{E1}+\mathcal{H}_{M1}|g\rangle|^2 - |\langle e_\uparrow|\mathcal{H}_{E1}-\mathcal{H}_{M1}|g\rangle|^2\\ &= 2\langle g|\mathcal{H}_{M1}|e_\uparrow\rangle\langle e_\uparrow|\mathcal{H}_{E1}|g\rangle + 2\langle g|\mathcal{H}_{E1}|e_\uparrow\rangle\langle e_\uparrow|\mathcal{H}_{M1}|g\rangle\\ &= 2(1+\cos\theta)\mathrm{Re}(\langle s_\uparrow|\mathcal{H}_{M1}|e_\uparrow\rangle\langle e_\uparrow|\mathcal{H}_{E1}|s_\uparrow\rangle)\\ &\quad + 2(1-\cos\theta)\mathrm{Re}(\langle s_\downarrow|\mathcal{H}_{M1}|e_\uparrow\rangle\langle e_\uparrow|\mathcal{H}_{E1}|s_\downarrow\rangle)\\ &\quad + 2\sin\theta\,\mathrm{Re}(e^{i\phi}\langle s_\uparrow|\mathcal{H}_{M1}|e_\uparrow\rangle\langle e_\uparrow|\mathcal{H}_{E1}|s_\downarrow\rangle)\\ &\quad + 2\sin\theta\,\mathrm{Re}(e^{-i\phi}\langle s_\downarrow|\mathcal{H}_{M1}|e_\uparrow\rangle\langle e_\uparrow|\mathcal{H}_{E1}|s_\uparrow\rangle). \qquad (3)\end{aligned}$$

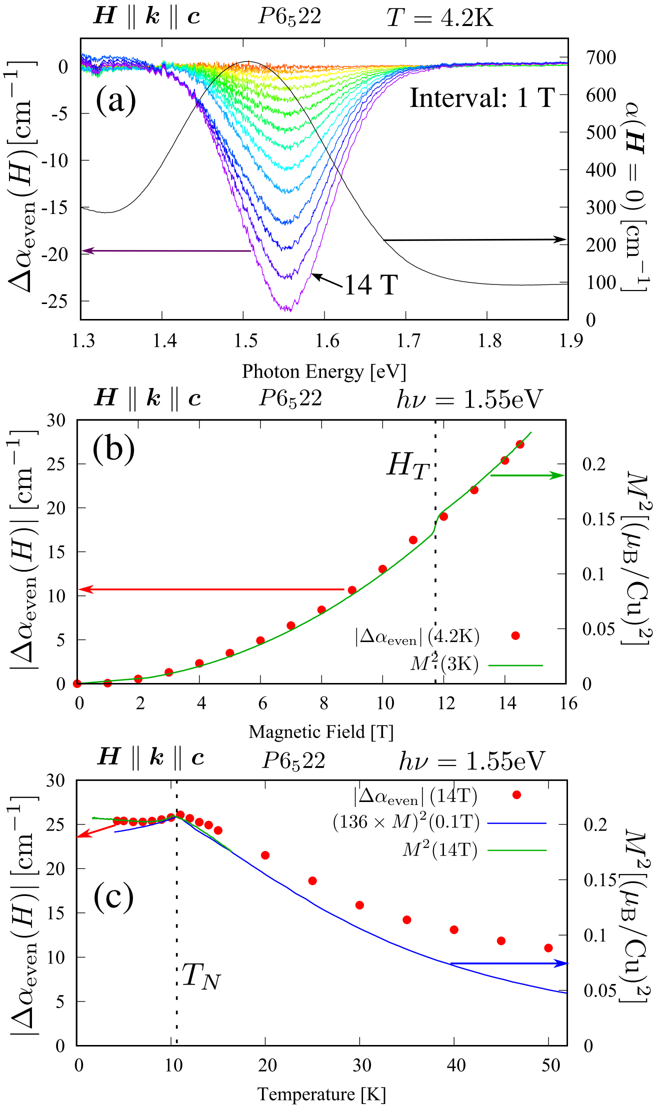

FIG. 4. H-even component of absorption coefficient change $\Delta\alpha_{\mathrm{even}}$, which is regarded as the Cotton-Mouton effect. (a) $\Delta\alpha_{\mathrm{even}}$ spectrum with $H = 1$–14 T (color lines) and absorption coefficient (black line). (b) The magnetic-field dependence of the H-even component at 1.55 eV (red circles). The green curve shows the square of the magnetization M^2. (c) Temperature dependence of the H-even component at 1.55 eV (red circles). The temperature dependence of M^2 is also drawn as a green line lower than 15 K. Blue lines show the temperature dependence of M^2 at 0.1 T to estimate the M^2-T graph in the paramagnetic phase.

These calculations are described in detail in the Supplemental Material [26]. Because $CsCuCl_3$ has an incommensurate spin screw around the c axis below T_N, the summation of MChD for all of the Cu atoms is equal to integrating ϕ: $0 \rightarrow 2\pi$. Because the latter terms of Eq. (3), which contain ϕ, cancel out, $\Delta\alpha_\uparrow$ is written as the linear expression of $\cos\theta$. By substituting $A = 2\,\mathrm{Re}(\langle s_\uparrow|\mathcal{H}_{M1}|e_\uparrow\rangle\langle e_\uparrow|\mathcal{H}_{E1}|s_\uparrow\rangle)$ and $B = 2\,\mathrm{Re}(\langle s_\downarrow|\mathcal{H}_{M1}|e_\uparrow\rangle\langle e_\uparrow|\mathcal{H}_{E1}|s_\downarrow\rangle)$, $\Delta\alpha_\uparrow$ is simplified as

$$\begin{aligned}\Delta\alpha_\uparrow &\propto (1+\cos\theta)A + (1-\cos\theta)B\\ &= (A+B) + (A-B)\cos\theta. \qquad (4)\end{aligned}$$

$|e_\uparrow\rangle$ is converted to another excited state $|e_\downarrow\rangle$, which is separated from $|e_\uparrow\rangle$ by Zeeman splitting. Introducing the time-reversal operator T ($T\,|e_\uparrow\rangle = -\,|e_\downarrow\rangle$ and $T\,|e_\downarrow\rangle = |e_\uparrow\rangle$), the transition from $|g\rangle$ to $|e_\downarrow\rangle$ can be transformed as

$$\begin{aligned}\langle e_\downarrow|\mathcal{H}_{E1} + \mathcal{H}_{M1}|g\rangle &= \langle e_\downarrow|T^{-1}\{T(\mathcal{H}_{E1} + \mathcal{H}_{M1})T^{-1}\}T|g\rangle\\ &= \langle e_\uparrow|\mathcal{H}_{E1} - \mathcal{H}_{M1}|g'\rangle\,. \end{aligned}\qquad (5)$$

Here, $|g'\rangle\,(= T\,|g\rangle)$ is the wave function of the time-reversed initial state. The conversion from $|g\rangle$ to $|g'\rangle$ is equivalent to coordinate conversion, $\theta \to \pi - \theta$, $\phi \to \pi + \phi$. The sign of $\mathcal{H}_{M1}$ is inverted by applying the time-reversal operator. The sign of $\Delta\alpha_\downarrow$ (the magnitude of MChD for the transition to $|e_\downarrow\rangle$) should also be inverted because it consists of products of $E1$ and $M1$ terms. $\Delta\alpha_\downarrow$ can be described as

$$\begin{aligned}\Delta\alpha_\downarrow &\propto -\{(A+B) + (A-B)\cos(\pi - \theta)\}\\ &= -(A+B) + (A-B)\cos\theta. \end{aligned}\qquad (6)$$

If the Zeeman splitting is sufficiently small, the magnitude of the total MChD can be written as

$$\Delta\alpha_\uparrow + \Delta\alpha_\downarrow \propto 2(A-B)\cos\theta \propto M. \qquad (7)$$

Here, an incommensurate conical magnetic order is assumed. It appears that the correlation between M is retained in the paramagnetic phase or the coplanar magnetic phase because the distribution of ϕ is uniform. The terms in $\Delta\alpha_\uparrow$ and $\Delta\alpha_\downarrow$, including ϕ, may be canceled out. If $|e\rangle$ is composed of a single quantum state represented by a real function, MChD would not appear because the products of $E1$ and $M1$ transitions, such as $\langle s_\uparrow|\mathcal{H}_{M1}|e_\uparrow\rangle\,\langle e_\uparrow|\mathcal{H}_{E1}|s_\uparrow\rangle$, would be purely imaginary. Considering the space-inversion operator, it can be explained that the signs of MChD in $P6_122$ and $P6_522$ crystals are opposite to each other.

Apart from the magnetic-field-odd MChD effect, another optical effect even to the magnetic field was also observed. The even magnetic-field-modulated component $\Delta\alpha_{\text{even}}$ of the absorption coefficient can be calculated by

$$\Delta\alpha_{\text{even}}(H) = \frac{\alpha(H,+k) + \alpha(H,-k)}{2} - \alpha(H=0). \qquad (8)$$

Figure 4(a) shows the spectrum of $\Delta\alpha_{\text{even}}(H)$ in left-handed CsCuCl_3. The $\Delta\alpha_{\text{even}}$ spectrum of right-handed ($P6_122$) CsCuCl_3 is shown in the Supplemental Material [26]. There is a peak at 1.55 eV, while the peak of the absorption coefficient spectrum is at 1.5 eV. The $\Delta\alpha_{\text{even}}$ spectrum is clearly different from the differential of the absorption spectrum $d\alpha/d\omega$, and this deviation suggests the presence of another energy level. This component is always negative without depending on the signs of $\boldsymbol{k}$ or the chirality of the sample. The magnitude of $\Delta\alpha_{\text{even}}$ is proportional to the square of the magnetization [Fig. 4(b)]. The temperature dependence does not agree with the M^2-T curve over T_N. The $\Delta\alpha_{\text{even}}$ effect is related to the Cotton-Mouton effect. However, the sign of the Cotton-Mouton effect cannot be reversed by space inversion or the time-reversal operation. This property is consistent with $\Delta\alpha_{\text{even}}$. The second-order perturbation of the magnetic field between excited states, which is irrelevant to the magnetization, may be related to the Cotton-Mouton effect.

In conclusion, the magneto-chiral dichroism of CsCuCl_3 was successfully observed. The MChD signal of 0.3% per T was larger than has been reported to date in the paramagnetic phase at the near-infrared region. The magnitude of MChD was proportional to the magnetization regardless of the magnetic-phase transitions. This behavior was explained using a simple CuCl_6 cluster model.

This work was performed using the facilities of the High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University (Project No. 16H0023). This work was supported by JSPS KAKENHI Grants No. JP25220803, No. JP16H01065, and No. JP26800167.

---

[1] G. Wagnière and A. Meier, Chem. Phys. Lett. **93**, 78 (1982).
[2] G. L. J. A. Rikken and E. Raupach, Nature (London) **390**, 494 (1997).
[3] G. L. J. A. Rikken and E. Raupach, Nature (London) **405**, 932 (2000).
[4] Y. Kitagawa, H. Segawa, and K. Ishii, Angew. Chem., Int. Ed. **50**, 9133 (2011).
[5] C. Train, R. Gheorghe, V. Krstic, L. Chamoreau, N. S. Ovanesyan, G. L. J. A. Rikken, M. Gruselle, and M. Verdaguer, Nat. Mater. **7**, 729 (2008).
[6] G. L. J. A. Rikken and E. Raupach, Phys. Rev. E **58**, 5081 (1998).
[7] G. Kopnov and G. L. J. A. Rikken, Rev. Sci. Instrum. **85**, 053106 (2014).
[8] J. Goulon, A. Rogalev, F. Wilhelm, C. Goulon-Ginet, P. Carra, D. Cabaret, and C. Brouder, Phys. Rev. Lett. **88**, 237401 (2002).
[9] R. Sessoli, M. Boulon, A. Caneschi, M. Mannini, L. Poggini, F. Wilhelm, and A. Rogalev, Nat. Phys. **11**, 69 (2014).
[10] S. Kibayashi, Y. Takahashi, S. Seki, and Y. Tokura, Nat. Commun. **5**, 4583 (2014).
[11] M. Saito, K. Ishikawa, K. Taniguchi, and T. Arima, Phys. Rev. Lett. **101**, 117402 (2008).
[12] Y. Okamura, F. Kagawa, S. Seki, M. Kubota, M. Kawasaki, and Y. Tokura, Phys. Rev. Lett. **114**, 197202 (2015).
[13] S. Hirotsu, J. Phys. C **10**, 967 (1977).
[14] K. Adachi, N. Achiwa, and M. Metaka, J. Phys. Soc. Jpn. **49**, 545 (1980).
[15] H. Nojiri, Y. Tokunaga, and M. Motokawa, J. Phys. (Paris) **49**, C8 (1988).
[16] A. Miyake, J. Shibuya, M. Akaki, H. Tanaka, and M. Tokunaga, Phys. Rev. B **92**, 100406(R) (2015).
[17] A. Sera, Y. Kousaka, J. Akimitsu, M. Sera, T. Kawamata, Y. Koike, and K. Inoue, Phys. Rev. B **94**, 214408 (2016).
[18] H. Ohta, S. Imagawa, M. Motokawa, and H. Tanaka, Physica B **201**, 208 (1994).
[19] U. Schotte, N. Stüsser, K. D. Schotte, H. Weinfurter, H. M. Mayer, and M. Winkelmann, J. Phys.: Condens. Matter. **6**, 10105 (1994).
[20] H. Tanaka, U. Schotte, and K. D. Schotte, J. Phys. Soc. Jpn. **61**, 1344 (1992).

[21] Y. Tazuke, H. Tanaka, K. Iio, and K. Nagata, J. Phys. Soc. Jpn. **50**, 3919 (1981).

[22] H. Hyodo, K. Iio, and K. Nagata, J. Phys. Soc. Jpn. **50**, 1545 (1981).

[23] H. Ohsumi, A. Tokuda, S. Takeshita, M. Takata, M. Suzuki, N. Kawamura, Y. Kousaka, J. Akimitsu, and T. Arima, Angew. Chem., Int. Ed. **52**, 8718 (2013).

[24] Y. Kousaka, T. Koyama, M. Miyagawa, K. Tanaka, J. Akimitsu, and K. Inoue, J. Phys.: Conf. Ser. **502**, 012019 (2014).

[25] K. Momma and F. Izumi, J. Appl. Crystallogr. **44**, 1272 (2011).

[26] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.96.121102 for details of the quantum spin excitation calculation of magneto-chiral dichroism and sample dependence which were not referred to in this Rapid Communication.

[27] M. Saito, K. Taniguchi, and T. Arima, J. Phys. Soc. Jpn. **77**, 013705 (2008).

[28] S. Toyoda, N. Abe, S. Kimura, Y. H. Matsuda, T. Nomura, A. Ikeda, S. Takeyama, and T. Arima, Phys. Rev. Lett. **115**, 267207 (2015).

[29] S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition Metal Ions in Crystals* (Academic Press, New York, 1970), p. 106.

[30] R. Laiho, M. Natarajan, and M. Kaira, Phys. Status Solidi A **15**, 311 (1973).