Magnetic Control of Crystal Chirality and the Existence of a Large Magneto-Optical Dichroism Effect in CuB_2O_4

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The possibility of a magnetic field controlling the chirality of matter has been debated for a long time. Here, we report the successful induction of chirality in the noncentrosymmetric canted antiferromagnet, CuB_2O_4, by application of a low intensity static magnetic field. The chirality is reversed by a 90° rotation of the direction of the magnetic field. The induction of chirality by a magnetic field gives rise to a gigantic enhancement of magnetochiral dichroism in this material. The ability to switch handedness in combination with this large magnetochiral optical effect allows us to design new optical devices such as a magnetically controllable isolator.

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The question of whether a magnetic field can control the chirality of matter has been debated since the 19th century, because of its importance to the problem of the origin of life. Although there are many successful methods for affecting chirality [1–11], such as irradiation by circularly polarized light and magnetochiral photochemistry, the influence of magnetic fields remains to be determined. From the viewpoint of symmetry, a magnetic field alone cannot induce homochirality [5–7,11]. A magnetic field breaks time-reversal symmetry but not the space inversion associated with chirality. Therefore, one cannot switch chirality by the reversal of a magnetic field. Here, we report the induction of chirality in CuB_2O_4 by a magnetic field alone. Furthermore, the chirality is switched not by the reversal but by a 90° rotation of the field direction. We have also observed the magnetochiral dichroism which a chiral material is expected to exhibit in a magnetic field. The magnitude of the magnetochiral dichroism shows an extraordinarily large enhancement due to resonance with an intra-atomic *d-d* excitation in Cu. The spin-orbit coupling in Cu^{2+} ions plays an essential role in the magnetic induction of chirality and gigantic magnetochiral dichroism.

CuB_2O_4 has a bright blue color and crystallizes with a noncentrosymmetric but achiral tetragonal space group $I\bar{4}2d$ [12]. Magnetic Cu^{2+} ions occupy square planar Cu (*A*) sites and distorted octahedral Cu (*B*) sites, as shown in Fig. 1(a). Because four Cu *A* sites in a unit cell have different *z* coordination, the Cu sites form an equal number of left- and right-handed screws propagating along the *c* axis with a periodicity of the crystallographic unit cell, as depicted by the circular arrows in Fig. 1(b). In other words, the crystal can be regarded as "racemic." CuB_2O_4 undergoes successive magnetic transitions at 10 and 21 K [13–17]. Between 10 and 21 K, the magnetic moments at the *A* sites show commensurate easy-plane antiferromagnetism with a canted ferromagnetic component along the [110] axis due to the Dzyialoshinskii-Moriya interaction [14,15,18,19]. The canting angle of magnetic moments is reported to be 3°. The magnetic group is $2'mm'$ [15,18], indicating the achiral nature of this magnetic phase, as shown in Fig. 1(d). However, the application of a magnetic field along the *a* axis aligns the Cu (*A*-site) magnetic

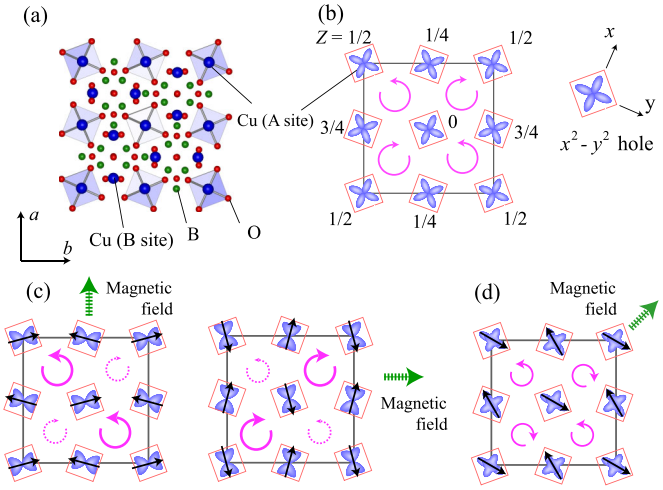

FIG. 1 (color online). Crystal and magnetic structures in CuB_2O_4 at 12 K. (a) (001) plane projection of the crystal structure in CuB_2O_4. Small spheres represent oxygen and boron atoms. Cu atoms (large spheres) occupy two inequivalent positions: *A* sites and *B* sites. Cu atoms on the *A* sites are surrounded by four oxygen atoms, as shown by squares. (b) The alignment of Cu^{2+} ions on the *A* sites. The *z* positions are given by fractional numbers. The Cu ions form right- and left-handed screws shown by circle arrows. A hole occupies an $x^2 - y^2$ orbital at each Cu^{2+} (*A*-site) ion. (c) Arrangements of spin moments (black arrows) in the canted antiferromagnetic phase of CuB_2O_4 in a magnetic field applied in the directions shown by dashed arrows. Canting of Cu (*A*-site) spin moments is exaggerated. Deformation of hole clouds by the spin-orbit coupling at *A* sites is depicted schematically. As a consequence, the right- and left-handed screws become inequivalent (solid and dotted circle arrows). (d) The application of a magnetic field parallel to the [110] axis does not affect the racemic nature of the crystal.

moments nearly (anti)parallel to the b axis due to the predominant antiferromagnetic ordering, as shown in Fig. 1(c). As a result, the magnetic field breaks the diagonal glide planes and changes the magnetic point group to enantiomorphous $2'22'$ [18]. Another important prediction based on group theory is the controllability of the magnetically induced chirality. The two types of spin alignments in Fig. 1(c) are connected with each other by a diagonal diamond glide reflection which does not change the basic atomic positions. This implies that a 90° rotation of the magnetic field can switch the chirality.

CuB_2O_4 bulk single crystals were grown by a flux method [20]. The crystals were cut into thin plates with broadest surfaces of $(\bar{1}10)$ or (010) or (001). The thickness of every sample was 0.1 mm. Circular dichroism (CD) was investigated using a polarization-modulation technique and a phase-sensitive detection method [21]. A dc magnetic field was applied perpendicular to the propagation vector $\boldsymbol{k}$ of the light. The circular dichroism $\Delta\alpha t$ was calculated from a $1f$ signal, deduced by a lock-in amplifier, divided by the average intensity. Magnetochiral dichroism and optical magnetoelectric effects [18] were measured by detecting the change in transmittance with respect to a reversal of the dc magnetic-field direction in Faraday ($\boldsymbol{H} \parallel \boldsymbol{k}$) and Voigt ($\boldsymbol{H} \perp \boldsymbol{k}$) configurations, respectively. The total Faraday rotation of the quartz windows was about 0.01° and negligible in this study.

CD is known to be the most powerful tool for investigating the chirality of matter. Figure 2(a) shows CD spectra with the application of magnetic fields in various directions. Note that the light propagates along the c axis and perpendicular to the magnetic field (the so-called Voigt configuration), where conventional magnetic circular dichroism cannot emerge. Nevertheless, a clear CD signal shows up in a magnetic field along the a or b axis, as expected from the discussion above. The CD signal reverses under a 90° rotation of the field direction around the c axis. It is noteworthy that the CD spectrum is essentially unchanged by the reversal of magnetic field, consistent with the group theory argument mentioned above. The application of a magnetic field along the [110] axis should restore the glide mirror symmetry. In fact, there is little difference in absorbance between right and left circularly polarized light, as shown in Fig. 2(f).

It is known that a chiral medium can exhibit a unique magneto-optical effect termed magnetochiral dichroism (MCHD), which is a change in absorption depending on the scalar product of the magnetic field $\boldsymbol{H}$ and the light propagation vector $\boldsymbol{k}$ and which is essentially independent of the polarization state of light [9–11,22–26]. MCHD is clearly distinct from the conventional magneto-optical effects, termed magnetic circular dichroism (MCD), and the Voigt effect. MCD is the difference in absorption between left- and right-handed circularly polarized light in the presence of a magnetic field in the Faraday configuration.

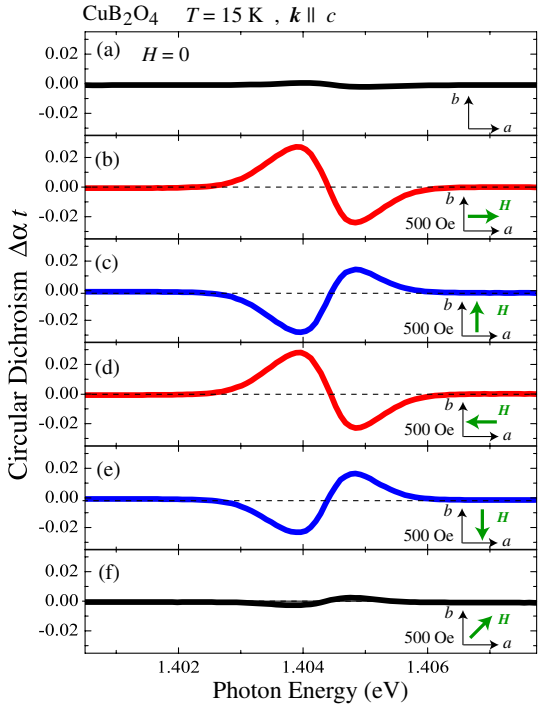

FIG. 2 (color online). Spectra of circular dichroism near the photon energy corresponding to a d-d transition at Cu (A) sites ($h\nu = 1.405$ eV) for various magnetic-field directions at 15 K. Left and right circularly polarized light propagates along the c axis. $\Delta\alpha t$ is the difference in absorption between the two polarizations. The direction of the applied magnetic field (H) of 500 Oe is indicated by an arrow in each figure.

The Voigt effect is the magnetic linear birefringence or dichroism in the presence of a magnetic field in the Voigt configuration. The appearance of MCHD provides further evidence for the magnetic induction of chirality in CuB_2O_4. Figure 3(b) shows the MCHD spectrum for unpolarized light in a magnetic field of 500 Oe applied along the b axis at 15 K. It should be remembered that the chirality in CuB_2O_4 is unchanged by the reversal of the field direction. Sharp MCHD peaks are discernible at $h\nu =$ 1.405, 1.67, and 1.91 eV, corresponding to the zero-phonon absorption lines of intra-atomic d-d transitions in the A-site Cu^{2+} ions, as shown in Fig. 3(a) [27]. We also measured a dichroism related to the magnetochiral effect with light polarized parallel to the a axis, because the tetragonal crystal originally has a large linear dichroism. Comparing the dichroism in Faraday configuration for linearly polarized light [Fig. 3(c)] to that for unpolarized light [Fig. 3(b)], the overall features remain the same and the magnitude of the signal becomes larger. This indicates that the MCHD shown in Fig. 3(b) should be attributed to the change in the absorption of light polarized parallel to the basal (001) plane under a reversal of the magnetic field. To confirm that this signal should be ascribed to the MCHD effect, we measured the dichroism in the Voigt configuration for the same sample. The dichroic signal almost

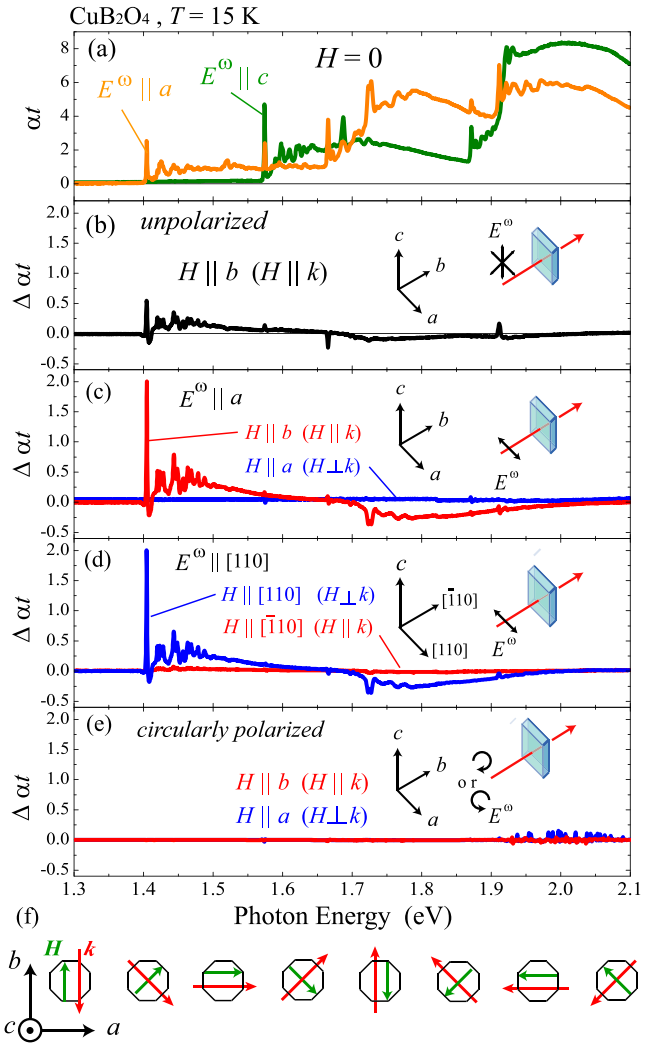

FIG. 3 (color online). (a) Absorption spectra in zero magnetic field for light polarized along the a axis and the c axis. (b) Spectrum of magnetochiral dichroism for unpolarized light propagating along the b axis. The magnetic field is applied parallel or antiparallel to the propagation vector $\boldsymbol{k}$. (c), (d) Spectra of magneto-optical effects for the various configurations given in the insets. $\Delta\alpha t$ denotes the change in absorption coefficient under a reversal of the magnetic field of 500 Oe. (e) Spectra of circular dichroism in the Faraday and Voigt configurations, respectively. (f) A possible optical "rotary switch" made from an octagonal prism shaped single crystal of CuB_2O_4. Short and long arrows indicate the directions of an external magnetic field and directions with the smallest absorption, respectively.

vanishes for $H \perp k$, as shown in Fig. 3(c). The dichroism is, therefore, evidently induced by the magnetic field parallel to $\boldsymbol{k}$ [28]. Moreover, giant MCHD cannot be observed in a magnetic field parallel to the $[\bar{1}10]$ axis in Faraday configuration [Fig. 3(d)], as expected from the fact that a field in this direction does not induce chirality.

Generally, MCHD is expected to be a rather small effect [25,26], because it is intuitively regarded as a product of CD and MCD [9,12,24]. In CuB_2O_4, both CD [Fig. 2 and a dark line in Fig. 3(e)] and MCD [a light line in Fig. 3(e)] are much smaller than MCHD. MCHD in CuB_2O_4 for light polarized perpendicular to the c axis probably arises from the interference between an electric dipole ($E1$) transition with an in-plane electric field $\boldsymbol{E}^\omega \perp c$ and a magnetic dipole ($M1$) transition with an out-of-plane magnetic field $\boldsymbol{H}^\omega \parallel c$. In fact, the observed MCHD spectrum is quite similar to the gigantic optical magnetoelectric dichroism displayed in Fig. 3(d) [18], which has been attributed to the interference between an $E1$ transition with $\boldsymbol{E}^\omega \perp c$ and an $M1$ transition with $\boldsymbol{H}^\omega \parallel c$ [18,29]. The extraordinarily large MCHD in CuB_2O_4 should also be understood based on the interference between the comparable $E1$ and $M1$ transitions. This is in contrast to CD, which is caused by the interference between $E1$ and $M1$ transitions with $\boldsymbol{E}^\omega \parallel \boldsymbol{H}^\omega$. Cu^{2+} ions with a $3d_{x^2-y^2}$ hole at the planar square sites should cause the relevant $E1$ and $M1$ transitions to be anisotropic. As a result, MCHD is not directly connected with CD and MCD and can be very large.

The value of the absorption coefficient (α) increases by a factor of 3 with a change of magnetic field from -300 to 300 Oe, as shown in Fig. 4(d). The strong magnetic-field dependence of α allows us to record the MCHD as a large change in the transmission of light, which is interesting from the viewpoint of possible applications for novel optical devices such as a magnetically controllable optical isolator and switch. For example, a single crystal of CuB_2O_4 with an octagonal prism could work as an optical switch with interesting properties. Figure 3(f) shows the directions in which light can be transmitted with the small-

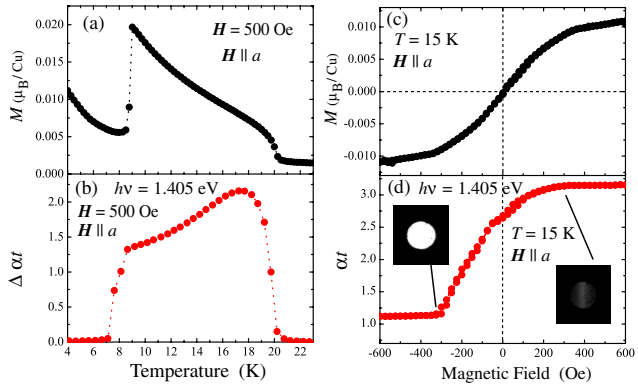

FIG. 4 (color online). Temperature evolutions of (a) MCHD at $h\nu = 1.405$ eV and (b) magnetization of CuB_2O_4 in a magnetic field of 500 Oe along the b axis. Polarization of $\boldsymbol{E}^\omega$ is parallel to the a axis. $\Delta\alpha$ denotes the change in absorption coefficient with respect to a reversal of the magnetic field. Magnetic-field dependence of (c) absorption α at $h\nu = 1.405$ eV and (d) magnetization of CuB_2O_4 at 15 K measured after zero-field cooling. Insets in (d) show images of light transmitted through a (010)-plate sample in magnetic fields of -300 and 300 Oe recorded by a CCD camera. The exposure time is 0.1 s. Both photographs are displayed with the same brightness and contrast.

est absorption (long arrows) for various orientations of the magnetic field (short arrows). A clockwise rotation of the magnetic field results in a counterclockwise rotation of the direction with the largest transmission.

Finally, we discuss the microscopic mechanism of the magnetic induction of chirality. Figure 4 shows the temperature evolution of the MCHD intensity as well as magnetization in a magnetic field of 500 Oe along the a axis. The large MCHD signal appears only in the collinear antiferromagnetic phase, and even in this phase, the magnitude of the MCHD changes in the opposite way to the magnetization. This temperature dependence strongly suggests that the crystal chirality is closely related to the antiferromagnetic component of Cu (A-site) spin moments. The hole spin lying in the square plane will modify the fourfold symmetry of the $x^2 - y^2$ hole density distribution through spin-orbit interactions. For example, when the spin is in the $x + y$ direction, the $(x + y)z$ orbital is hybridized with the $x^2 - y^2$ orbital. The spin alignment and the consequent modulation of the hole distribution in a magnetic field are schematically drawn in Figs. 1(c) and 1(d). Only when a magnetic field is applied along the a or b axis do the right- and left-handed screws become inequivalent, resulting in chirality. Comparing the two panels in Fig. 1 (c), we see that the chirality induced by the modified hole distribution at the A sites is reversed by a 90° rotation of all the spin moments, which is realized by a 90° rotation of the magnetic-field direction. The hole orbitals are also modified in a magnetic field along the [110] axis. Nevertheless, right- and left-handed screws remain equivalent as shown Fig. 1(d). In fact, the point group asserts that right- and left-handed screws are interchangeable with a glide reflection.

In summary, we have succeeded in inducing chirality in CuB_2O_4 by the application of a magnetic field. The chirality can be easily reversed by changing the magnetic-field direction. Such magnetic induction and control of chirality can be realized in all magnets with a point group $\bar{4}2m$, such as $Ga_{1-x}Mn_xAs$ film on a (001) substrate and $Ba_2CoGe_2O_7$. This will open the door to a new paradigm of magnetically switchable enantioselective catalysis. In the magnetically induced chiral state of CuB_2O_4, gigantic magnetochiral dichroism is observed. This is due to resonance with magnetic dipole-allowed intra-atomic d-d excitations. The amount of the observed magnetochiral dichroism is in the range of the total absorption for the $\sim$1.405 eV transition of Cu^{2+}. The signal is approximately 4 orders of magnitude larger than any previously reported MCHD [9]. The extraordinary enhancement may provide the potential for the development of magneto-optical devices. In addition, the present discovery of a relation between chirality as an important property of life and magnetic fields on earth has relevance to the problem of the origin of life.

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