Magnetic Circular Dichroism in X-Ray Emission from Ferromagnets

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The existence of novel magnetic circular dichroism in core-level x-ray emission is reported. By means of circular polarization analysis, the dichroic effect of the Fe $K\alpha_1$ emission spectrum is measured on an Fe single crystal. The observed dichroic effect (12%) is remarkably large, if one takes into account the small dichroic effect (about 0.5%) in the conventional K-edge absorption spectroscopy of $3d$ transition metal elements. The mechanism is ascribed to exchange splitting of the $2p$ level possessing large spin-orbit coupling. This new magnetooptical effect enables us to explore a variety of new research subjects in the magnetism of $3d$ transition metals and their compounds by fully utilizing its large dichroic effect, the true bulk sensitivity of hard x rays, and the element selectivity of core-level spectroscopy.

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X-ray magnetic circular dichroism (XMCD) is defined as the difference in absorption cross section between right and left circularly polarized x rays that impinge on a magnetized material. Since the dichroic signal is resonantly enhanced near the absorption edges of elements, XMCD is an inherently element-selective technique. In addition, XMCD is currently so sensitive that it can measure tiny magnetic moments and small-volume samples [1,2]. Furthermore, at spin-orbit split absorption edges, the orbital and spin contributions to the total magnetization are separately and quantitatively evaluated through the application of magnetooptical sum rules [3,4]. The combination of these characteristic features makes XMCD a useful and powerful tool for research in both basic [5–7] and applied [8–10] magnetism.

A major disadvantage of XMCD is a very small dichroic effect for $3d$ transition metals (TMs), such as Fe, Co, and Ni, in the hard x-ray regime, despite that they are crucial elements in ferromagnetic materials. At the $L_{2,3}$ edges of these elements, which reside in the soft x-ray regime, the dichroic effect is quite large (typically about 30% in Fe and Co metals) [11]. This is one of the reasons that the magnetic properties of $3d$ TMs are generally investigated at the $L_{2,3}$ edges of these elements. The technique is surface sensitive when electron yield is employed, and the probing length is typically a couple of 100 nm when fluorescence yield or a transmission method is utilized. XMCD in the soft x-ray regime is thus suited for measuring surface magnetism or magnetic thin films. Accordingly, it is indispensable to use hard x rays for experiments that survey regions well below the surface of bulk magnetic materials or a sample in a container, such as a high-pressure cell. Nevertheless, the dichroic effect of $3d$ TMs at the K edges, which range from 5 to 9 keV in the hard x-ray regime, is extremely small (at most 0.5%) [12]. There exists a considerable demand to find a new principle that would make it possible to perform a bulk-sensitive XMCD measurement with a large dichroic effect for $3d$ TMs.

In this Letter, a new magnetooptical effect in the hard x-ray regime is proposed and is experimentally confirmed. A crucial feature of the phenomenon is that x rays emitted from a magnetized medium are circularly polarized. The new effect is an x-ray analogue of magnetic circularly polarized emission in the visible regime [13,14], and is thus distinct from conventional magnetooptical effects observed in transmission (Faraday effect), reflection (Kerr effect), and absorption (MCD) of light, in that circular dichroism is exhibited in the emission spectra of light. Experimentally, the degree of circular polarization is measured in the $K\alpha_1$ spectra (6.404 keV) emitted from an iron single crystal at room temperature. The obtained circular polarization is large (12%) and may amount to 18%, if necessary corrections are made, which is comparable to the dichroic effect of XMCD in the soft x-ray regime. A brief multiplet calculation is also made to assist the experimental observation.

Prior to proceeding to the experimental details, the basic idea of magnetic circular dichroism in x-ray emission proposed here is given below. A schematic is also shown in Fig. 1. In a simple model, the dichroic effect is proportional to the orbital polarization [15]. However, in the x-ray absorption process at the K edge of $3d$ TMs ($1s \rightarrow 4p$), the $4p$ orbital is empty and has no orbital polarization. Likewise, the $1s$ orbital has no orbital angular momentum in the first place. The dichroic effect of the K absorption process is thereby small in principle. In contrast, the $2p$ orbital, which is involved in the $K\alpha$-emission process ($2p \rightarrow 1s$), may have an orbital angular momentum. Because of large spin-orbit coupling, the final $2p^5$ state splits into a $2p_{1/2}$ doublet and a $2p_{3/2}$ quartet, where the $2p_{3/2} \rightarrow 1s$ process corresponds to the $K\alpha_1$ emission. The $2p_{3/2}$ quartet further splits owing to the spin polarization in the $3d$ orbital through the sizable $2p3d$ exchange

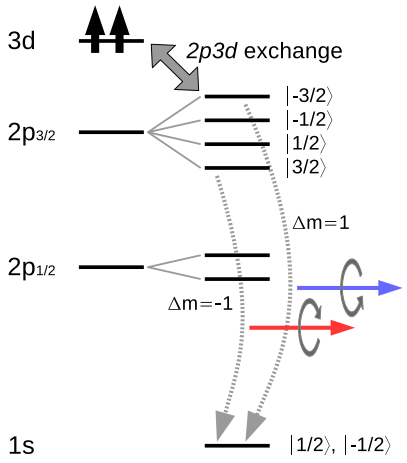

FIG. 1. (a) Energy-level diagram showing the origin of circular dichroism in x-ray emission. For clarity, two transitions are indicated among four $K\alpha_1$ transitions. The magnetic quantum number is shown in $2p_{3/2}$ and $1s$ sublevels. Δm is the change in magnetic quantum number at the transition.

interaction [16]. Although the exchange interaction affects only the spin state, since the orbital state tightly couples to the spin state in the $2p$ orbital, the spin polarization in the $3d$ orbital is eventually reflected to the orbital polarization on the energy-resolved $2p_{3/2}$ state. Accordingly, a large dichroic effect is expected in x-ray emission at the K edge of $3d$ TMs. Since the $2p3d$ exchange interaction is a perturbation to the $2p$ spin-orbit coupling, it is likely that the exchange splitting of the $2p_{3/2}$ levels is simply proportional to the spin polarization in the $3d$ orbital. Hence, it is expected that this new magnetooptical effect probes mainly the spin magnetization $\langle m_s \rangle$. Detailed calculations are necessary to confirm this point.

The measurements were carried out at BL22XU of SPring-8. The experimental setup is schematically illustrated in Fig. 2. Incident x rays generated from a planar undulator were monochromatized by a Si(111) double-crystal monochromator and were focused onto a sample by a pair of mirrors. The source size on the sample was restricted by an incident slit (slit 3), of which the aperture

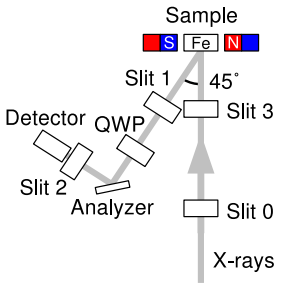

FIG. 2. Top view of the experimental layout. QWP: A diamond phase retarder that acts as a quarter-wave plate. Analyzer: A Ge(400) single crystal that is both an energy and polarization analyzer.

was 100 μm(H) × 75 μm(V). An exit slit (slit 1), which was placed about 600 mm downstream of the sample, collimated the emitted x rays. The aperture of slit 1 was 75 μm × 75 μm. The angle between the incident x rays and the emitted x rays was set to 45°. The divergence of the emitted x rays after the exit slit is thus expected to be about 120 μrad. A quarter-wave plate (QWP) placed after slit 1 was a 500 μm-thick single-crystal diamond plate with (100) surface orientation. This is a device that converts circularly polarized x rays to linearly polarized x rays [17] and was operated near the 220 reflection. A Ge (400) single crystal placed after the QWP functioned as both a polarization and energy analyzer. The scattering angle $2\theta_A$ at Fe $K\alpha_1$ was 86.4° so that only the vertical component of the x rays was effectively detected. The energy resolution ΔE is estimated to be 0.83 eV from $\Delta E/E = \cot\theta_A \Delta\theta$, where $\Delta\theta$ is the divergence of x rays incoming to the analyzer (120 μrad). The detector was a silicon drift detector (Amptek XR-100SDD). The sample was an iron single crystal, which was inserted between $Nd_2Fe_{14}B$ permanent magnets in order to saturate the magnetization. The magnetic field was about 0.5 T and was perpendicular to the incident x rays. The direction of the magnetic field was reversed by reversing the magnets. The spectra were recorded by simultaneously scanning the analyzer angle and the QWP angle. The incident photon energy was 7.13 keV (the white line of the Fe absorption spectrum) and the measurements were done at room temperature. The combination of a QWP and a polarization analyzer is a standard device that detects the circular polarization of a beam of photons [18]. In short, the device transmits right (left) circularly polarized x rays and 50% of linearly polarized x rays when the QWP generates a $\pi/2$ $(-\pi/2)$ phase shift.

The obtained Fe $K\alpha_1$ emission spectra are indicated in Fig. 3(a). The I^+ (red open circles) and I^- (blue closed circles) are data observed when the $\pi/2$ and $-\pi/2$ phase shifts are introduced by the QWP, respectively. The magnetic field is applied as shown in the inset and is defined as the positive direction. Although the statistics are somewhat poor, it is obvious that the I^+ and I^- spectra do not coincide with each other. The I^+ spectrum is shifted to the low-energy side by about 0.3 eV compared with the I^- spectrum. As described in the Supplemental Material [18], the difference between the two spectra is a direct measure of the circular polarization.

The difference spectrum $I^+ - I^-$ normalized by the peak intensity of the sum spectrum is shown in Fig. 3(b) as magenta solid circles. The spectrum exhibits the so-called derivative shape. By reversing the magnetic field, the tendency is reversed. The green open circles are data measured when the magnetic field is applied along the negative direction. These results unambiguously illustrate that (i) the energy-resolved $K\alpha_1$ spectrum of ferromagnetic Fe indicates finite circular polarization and (ii) the circular polarization is inverted when the magnetization of the

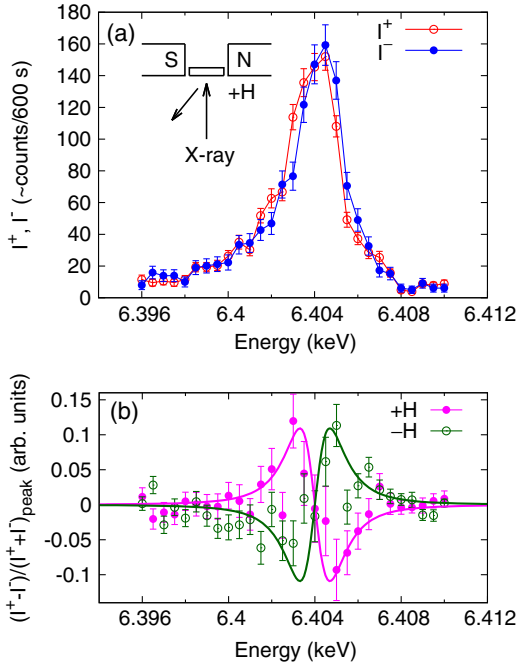

FIG. 3. (a) Fe $K\alpha_1$ emission spectra I^+ and I^- for a phase shift of $+\pi/2$ (red open circles) and $-\pi/2$ (blue solid circles), respectively. The lines connect the data points to guide the eye. The magnetic field is applied as shown in the inset and the direction is defined as positive. (b) Difference spectra between I^+ and I^- normalized by the peak intensity with two antiparallel directions of magnetic field. Magenta solid circles and green open circles are measured when the magnetic field is directed along the positive and negative direction, respectively. Solid lines are a guide to the eye. Note that the ordinate is not exactly the degree of circular polarization.

sample is inverted. These two features are evidence for the existence of XMCD in the Fe $K\alpha_1$ emission.

A flipping ratio is a measure of the size of the dichroic effect and is defined as

$$(I^+ - I^-)/(I^+ + I^-).$$

Note that the flipping ratio is equal to the degree of circular polarization here. The flipping ratio at 6.405 keV was measured with good statistics and was found to be $(12 \pm 4)\%$. If the correction about the scattering angle (0.71) and the efficiency of the QWP (0.93) are taken into account, the value would amount to $(18 \pm 6)\%$, which is comparable to that in the soft x-ray regime (about 30%). Accordingly, it is experimentally confirmed that the magnetic circular dichroism actually exists in x-ray core-level emission and that the dichroic effect is quite large even in the K edge of the $3d$ TMs.

XMCD in the $K\alpha$ emission is also supported by multiplet calculations. In this work, the CTM4XAS 5.5 program was used [19]. The initial and final states were $1s^1 3d^6$ and $2p^5 3d^6$, respectively. A choice between $3d^6$ and $3d^5$ states did not influence the results much; thus, the calculations for

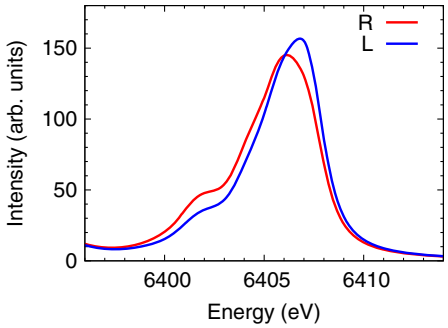

FIG. 4. Calculated Fe $K\alpha_1$ emission spectra. The red (blue) line corresponds to the sum of intensities for the right (left) circularly polarized x rays and one-half of the linearly polarized x rays. Dichroism is obvious in the theoretical calculations.

the $3d^6$ state are shown. The Slater integrals F_{dd}, F_{pd}, and G_{pd} were reduced down to 72% with respect to the Hartree-Fock values. The crystal field was set to $10Dq = 0.9$ eV [20] and the exchange field was set to $M = 7$ meV. The obtained spectra were broadened using a Lorentzian and a Gaussian function in order to account for the core-hole lifetime broadening and the instrumental energy resolution, respectively. The full widths at the half maximum of the Lorentzian and Gaussian functions were set to 1.5 and 0.84 eV, respectively. The calculated spectra are depicted in Fig. 4. The red (blue) line corresponds to the sum of intensities for the right (left) circularly polarized x rays and one-half of the linearly polarized x rays. Although the calculated spectra are somewhat broader than the observed and reported spectra [21], the difference between the two calculated spectra clearly illustrates that a large dichroic effect theoretically exists in the x-ray emission.

As shown above, both the experimental and theoretical results undoubtedly indicate that the K emission from ferromagnetic Fe is substantially circularly polarized. Hence, this magnetooptical effect may open a new way to perform element-selective and truly bulk-sensitive measurements of the magnetization. The very low count rate in this work can be overcome by introducing an optical device that converts a divergent beam to a well-collimated beam. Montel optics is an example of this type of collimating optical device [22]. If a collimating optical device with an acceptance angle of 5 mrad and a reflectivity of 20% is inserted between the sample and the phase plate, the detected intensity could be increased by about 200 times compared with that without such a device. This large enhancement of the intensity would make it possible to use this effect as a useful investigative tool. In particular, an advantage of this effect is the possibility to extend a probing depth compared with existing core-level spectroscopies. Since the excitation energy is arbitrary if it is higher than the absorption edge, high-energy x rays with large penetration power can be used for incident x rays. (The cross section for the creation of a $1s$ core-hole decreases, though.) In addition, the x-ray attenuation length for a sample

is generally longer at the fluorescence energy just below the absorption energy than that at the absorption edge. Therefore, a measurement of magnetic domains well below the surface of bulk magnetic materials would be a good application. Similarly, experiments under high pressure are also promising. In contrast, application of magnetooptical sum rules provides no information about the orbital and spin moments, because the $2p$ state is filled and thus has no orbital and spin moments in the ground state [23,24].

In the rest of the Letter, I would like to mention the similarities and differences between this magnetooptical effect and two related x-ray spectroscopies. One spectroscopy is MCD on resonant inelastic x-ray scattering (RIXS). RIXS is a coherent second-order optical process that combines photoabsorption and radiative decay. Similar to absorption XMCD, in which the dichroic effect is detected in the absorption cross section, the dichroic effect is observed in the intensity of the emitted x rays in RIXS by changing the helicity of the incoming x rays. This phenomenon, abbreviated as MCD/RIXS, was first reported in $3d$ TMs in the soft x-ray regime [25–28], and MCD/RIXS measurements were subsequently extended to rare-earth metals and alloys in the hard x-ray regime [23,29–32]. A huge enhancement of the dichroic effect is a particular feature of MCD/RIXS; for instance, a dichroic effect as high as 50% has been reported for a GdCo alloy [30]. Another feature is that MCD/RIXS utilizes spin dependence in the absorption process at the L edge [23]. Accordingly, no dichroic effect is expected at the K edge [33]. A sophisticated way that bypasses this difficulty is a RIXS technique that uses spin-dependent $1s \rightarrow 3d$ excitation at the preedge [34]. However, the lack of inversion symmetry at the TM site, which gives rise to $3d$-$4p$ hybridization, is practically required in this technique, because the strong enhancement of the preedge features through $1s \rightarrow 4p$ dipole transitions caused by the $3d$-$4p$ hybridization is efficiently utilized. In contrast, a rather straightforward solution to the problem is the polarization analysis of emitted x rays exhibited in this work.

The other spectroscopy is spin-selected x-ray absorption spectroscopy (SSXAS). In SSXAS, spin-dependent x-ray absorption spectra are obtained in samples with no long-range magnetic order without using circularly polarized x rays [35–40]. SSXAS, particularly on $3d$ TMs, is based on the assumption that in the $K\beta$ emission process ($3p \rightarrow 1s$) the spin direction of a decaying electron can be selected to be either parallel or antiparallel to the local $3d$ moment of the absorbing atom by tuning the emission energy. The exchange interaction between the $3p$ hole spin and the $3d$ moment splits the $K\beta$ emission into a main line ($K\beta_{1,3}$: spin down) and a satellite line ($K\beta'$: spin up) [20]. In addition, the spins of the excited electron, the decaying electron, and the $3p$ hole are all parallel because a dipole transition conserves the spin. Accordingly, one can obtain a spin-dependent absorption spectrum by monitoring either the $K\beta_{1,3}$ or $K\beta'$ emission as a function of incident x-ray energy. However, SSXAS cannot be an alternative to XMCD. SSXAS cannot measure the net magnetization of a sample in principle, because SSXAS is sensitive to only the internally referenced direction of the magnetic moment of the absorbing atom. Of course, the externally referenced direction of the moment can be resolved in SSXAS if one determines the spin direction of the decaying electron, by utilizing the Auger electron in Ref. [41] and by utilizing spin-orbit coupling in this work, for instance. From these comparisons, it turns out that a gap that differentiates the new magnetooptical effect from conventional x-ray spectroscopies is circular polarization analysis of emitted x rays.

To summarize, novel magnetic circular dichroism in x-ray emission is proposed and it is experimentally confirmed that characteristic x rays ($K\alpha_1$) emitted from ferromagnetic Fe are circularly polarized to a considerable extent. A large dichroic effect for TMs in the hard x-ray regime ensures that this new magnetooptical effect could be used in practical applications that take advantage of element specificity and bulk sensitivity. It would also be interesting to extend experiments to $K\beta$ emission in $3d$ TMs and $L\alpha$ and $L\beta$ emissions in lanthanides from the view point of spectroscopy.

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