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Strong magnetic circular dichroism at the $M_{2,3}$ edges in ferromagnetic Ni and ferrimagnetic Fe_3O_4

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Magnetic-circular-dichroism (MCD) spectra have been obtained at and around the $M_{2,3}$ core absorption edges in single crystals of ferromagnetic Ni and ferrimagnetic Fe_3O_4. Furthermore, strong MCD signals were observed for the weak multiplet structures of Fe_3O_4 in the prethreshold region. The experiments were performed using a bulk-sensitive reflection method by utilizing directly characterized, circularly polarized synchrotron radiation in conjunction with an ultrahigh-vacuum-compatible, i.e., bakable, superconducting magnet of special design. The present observation of a strong MCD not only provides a sensitive method for probing the local magnetic states of magnetic substances, but also could provide valuable information concerning the 3*d* electronic states of these materials.

Magnetic circular dichroism (MCD) in core-level absorption has recently attracted much interest. It provides insights into the element-specific local magnetic states of various magnetic materials, since the initial states involved in the optical transitions are well localized. This is in contrast to MCD spectra in the visible and near-ultraviolet regions where transitions take place between energy bands, thus making it difficult to directly correlate the spectral features to the spin-dependent electronic states.

Stimulated by the pioneering theoretical work of Erskine and Stern[1] as well as recent theoretical studies by Thole and co-workers,[2,3] a magnetic x-ray linear dichroism experiment was performed by van der Laan *et al.*[4] at the $M_{4,5}$ edges in a rare-earth compound. Magnetic x-ray circular dichroism (MXCD) measurements were subsequently carried out by Schütz *et al.*[5,6] and Collins *et al.*[7] at the K and $L_{2,3}$ absorption edges in magnetic transition metals, rare earths, and their compounds. MXCD studies have recently been extended down to the soft x-ray region by Chen *et al.*[8] New phenomenon of MXCD in core-level photoemission has also been observed by Baumgarten *et al.*[9] These experimental studies, in turn, stimulated many theoretical investigations[10–15] based on a variety of formalisms in order to provide an interpretation of the obtained spectra and, further, to obtain a more profound understanding of the magnetic properties.

All of the MCD experiments mentioned above[5–9] utilized circular polarization (CP) of off-plane synchrotron radiation (SR). However, calculated values of the degree of CP were relied upon. The magnetic fields applied to the samples were not always sufficiently high to saturate the sample magnetization. In addition, some of the experiments used a surface-sensitive technique rather than a bulk-sensitive method. These led to some doubts regarding the quantitative reliability of the data and/or difficulties in comparing theory and experiment.

No MCD experiment has apparently yet been reported regarding the $M_{2,3}$ edges in ferromagnetic 3*d* transition metals or their compounds, despite the first prediction of strong magneto-optical effects at these very edges in Ni by Erskine and Stern.[1] The main reason for this would be that the relevant transition energies (50–70 eV) fall into the intermediate region between normal- and grazing-incidence optics, thus requiring an experimental determination of the polarization state of light used for the MCD experiments at the sample position. The necessity of an UHV-compatible high-field magnet has also hindered such studies.

We have overcome these technical difficulties and are now able to successfully observe MCD at the $M_{2,3}$ edges in single crystals of ferromagnetic Ni and ferrimagnetic Fe_3O_4. Additionally, we have found unusually strong MCD signals for the weak multiplet structures in the prethreshold region of Fe_3O_4. This indicates the high sensitivity of these multiplets to the local magnetic state and, thus, could provide new possibilities for probing the electronic states related with the spin and orbital magnetism in many other magnetic substances. The present MCD study has the following threefold experimental characteristics, as compared with the previous MXCD experiments:[5–9] (i) the degree of CP was directly measured;

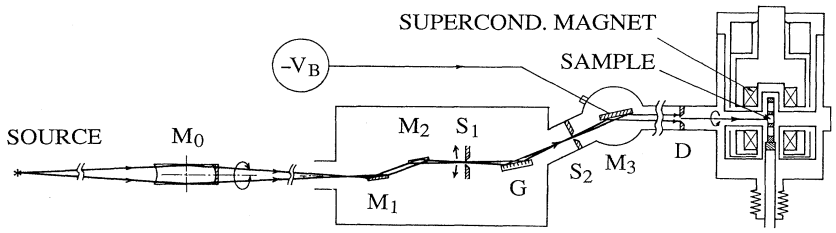

FIG. 1. Arrangement for the MCD experiments. Circular polarization was produced by deflecting the incoming beam vertically with respect to the entrance slit of the monochromator. M_0-M_3: mirrors; G: grating; S_1 and S_2: slits; D: diaphragm; $-V_B$: bias voltage.

(ii) the saturation of sample magnetization was experimentally confirmed by using an UHV-compatible superconducting magnet; and (iii) the bulk-sensitive reflection-MCD technique was utilized for single-crystal samples.

The experiments were performed using SR on beamline BL-11D at the Photon Factory, National Laboratory for High Energy Physics. Figure 1 shows a schematic view of the present experimental arrangement. Off-plane CP SR was extracted at the entrance slit of the monochromator (S_1) by deflecting the incoming beam vertically with the beamline first premirror (M_0). Since five optical elements (premirrors, a grating, and a postfocusing mirror) are used at nongrazing incidence between the light source and the exit port of the beamline, the degree of CP is difficult to estimate theoretically. Thus, the Stokes parameters,[16] which completely represent the polarization state of light, were measured for the emerging beam of the beamline prior to the MCD experiments. The measurements were made using a polarimeter comprising two triple-reflection polarizers in which the first polarizer acts as a phase shifter and the second one functions as a quasi-linear-polarization (LP) analyzer. Details regarding the production and measurement of CP will be reported elsewhere.[17] Figure 2 shows an example of the degree of CP, S_3/S_0, measured at 70 eV as a function of the deflection angle (θ_D). The degree of horizontal LP, S_1/S_0, is also shown for a comparison. Since the degree of CP (S_3/S_0) was not completely antisymmetric with respect to θ_D, the left-handed CP, denoted by an arrow, was used; instead, the magnetic field direction was switched. The degree of CP was -75%---85% over the 50–85-eV range. The movement of the beam center ($\theta_D = 0°$) was checked both before and after every single-sweep-spectrum measurement and was within $\frac{1}{40}$ mrad. The resultant change in the degree of CP was thus negligibly small.

The superconducting magnet is a split-coil solenoid producing fields of up to 5.8 T. The key aspect of this magnet system is a double-wall structure for a liquid-He cryosystem. This enables us to bake out the outer wall without any appreciable rise in the magnet temperature. Slight bakeouts have led to a pressure of $\sim 1\times10^{-9}$ Torr, sufficiently low for the present measurements.

The reflection-MCD technique was exploited with the Faraday configuration in normal-incidence (light incidence angle $= 4.3°$). A single crystal of Ni, purchased from Johnson Matthey Chemicals Ltd., had a purity of 99.999%. An Fe_3O_4 single crystal was prepared by a floating-zone technique in the ⟨111⟩ crystal orientation. Disks of ~ 10 mm in diameter and 2–3 mm in thickness were cut in the (111) surface from the crystal rods; the surface normal was coincident with the easy magnetization axis in both samples. They were mechanically polished to optical surfaces using diamond paste (as fine as 0.5 μm) with water used as the carrier. In order to suppress surface oxidation of the Ni sample as much as possible, it was further given a final slight polishing and immediately (within 1–2 min) put into a small vacuum chamber equipped with a vacuum pump and a valve. Sample mounting to the holder caused only a 10–20 min exposure to air just before measurements. The light reflected from the sample was detected with a sodium-salicylate-coated photomultiplier specially designed for use under high magnetic fields. The variation in the detector sensitivity was lower than 1% for a change in the magnetic field strength from 0 to 3 T; it was much less during switching of the field direction. A pinhole diaphragm D was placed in order to facilitate adjustments of the polarimeter axis to the beam axis and to reduce the scattered-light component. The output photon flux of the

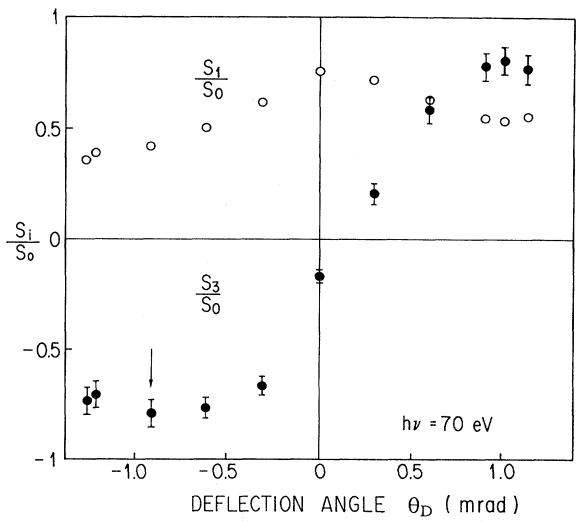

FIG. 2. Experimentally determined Stokes parameters of the emerging light of the beamline at 70 eV as a function of the beam-deflection angle (θ_D). The left-handed circular polarization (CP) denoted by an arrow was used for the MCD measurements. S_3/S_0: degree of CP; S_1/S_0: degree of horizontal linear polarization.

beamline was monitored using a photocurrent from the postfocusing mirror (M_3). A bias voltage of $-V_B \sim -150$ V was applied to the mirror so as to reject photoelectrons from diaphragm D as well as those from the sample which were transferred on the magnetic flux and transmitted through the pinhole of D. The monochromator slit width was set at 200 μm (resolution $\Delta E = 0.26$ eV at 60 eV).

Figure 3(a) shows the reflectance spectra of Ni for two opposite magnetization directions at a field strength of 0.5 T. Here, R_+ and R_- represent the reflectances involving transitions with $\Delta J_z = +1$ (σ_+) and $\Delta J_z = -1$ (σ_-) with the z axis taken in the direction opposite to the sample magnetization. Figure 3(b) displays the MCD spectrum, $\Delta R/R = (R_+ - R_-)/[(R_+ + R_-)/2]$, deduced from the spectra in Fig. 3(a). No background subtraction has been made for R_+ and R_-. A correction for the degree of CP ($|S_3/S_0| = 80\%$) has been made for the MCD spectrum. The MCD-signal intensity increased with the magnetic-field strength up to ~ 0.5 T; no appreciable change was observed over the 0.5–1.5-T range. This indicates the saturation of the sample magnetization at a field of ~ 0.5 T. Since $n \approx 1$ and $k \ll 1$ in this region (n and k are the real and imaginary parts of the complex refraction coefficient, respectively), reflection MCD gives essentially the same spectrum as does absorption MCD. A comparison of our reflectance spectra with the absorption spectra of Ni and NiO reported in the literature[18,19] showed that the influence of a surface oxide (NiO) was negligibly small; the present spectra clearly show bump B at ~ 78 eV, existing only in Ni, and no deep dip at the absorption maximum (~ 68 eV), which was observed only in NiO.

The MCD spectrum was found to exhibit a large negative peak at the M_3 edge, followed by a small positive peak at the M_2 edge with increasing energy. This marked asymmetry conflicts with the antisymmetric spectrum predicted by Erskine and Stern,[1] who took into account only the spin angular momentum of the $3d$ electrons on the basis of an augmented-plane-wave band calculation by Wang and Callaway.[20] The present result is in qualitative agreement with the MCD spectrum at the $L_{2,3}$ edges of Chen *et al.*[8] in that the MCD signal is negative in the threshold region and positive above it, and that the integrated MCD signal is negative. Jo and Sawatzky[13] have pointed out the importance of the orbital magnetic moment in interpretating the data of Chen *et al.*[8] Yoshida and Jo[21] have recently made a calculation of the MCD spectrum for the $M_{2,3}$ edges in Ni by taking account of the remaining orbital angular momentum. The present result is in agreement with their calculation, which incorporates an orbital magnetic moment of 0.08 μ_B.

Figures 4(a) and 4(b) show the results for Fe_3O_4 at a

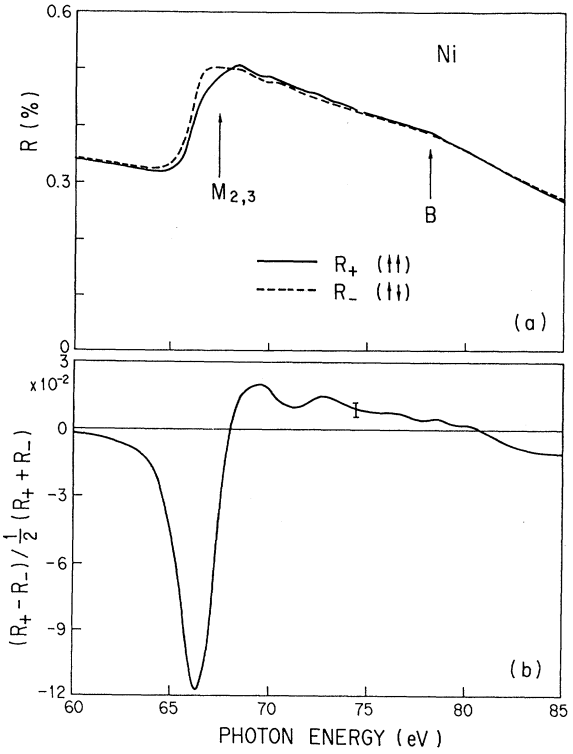

FIG. 3. (a) Reflectance spectra of Ni around the $M_{2,3}$ absorption edges for two different orientations between the spin direction of the incident photon and that of the majority $3d$ electrons. (b) MCD spectrum of Ni deduced from the spectra in (a).

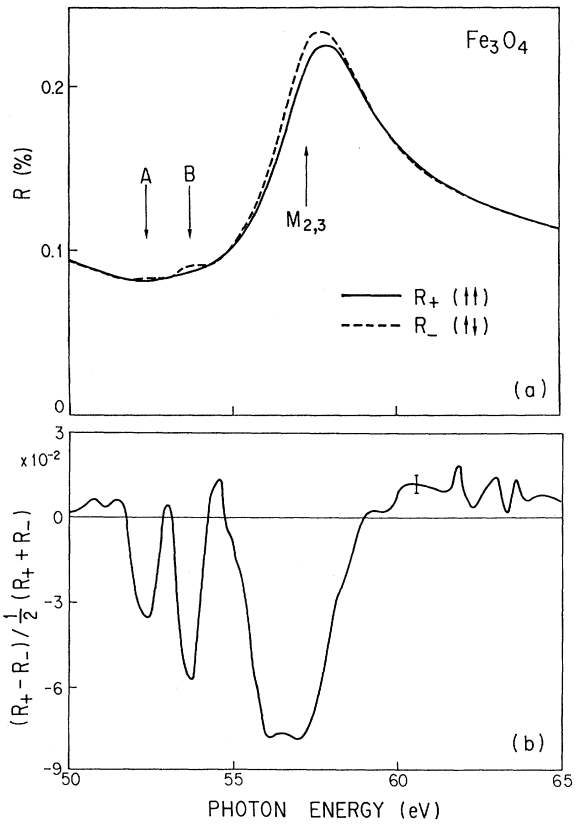

FIG. 4. (a) Reflectance spectra of Fe_3O_4 around the $M_{2,3}$ absorption edges in Fe for two different orientations between the spin direction of the incident photon and that of the majority $3d$ electrons. (b) MCD spectrum of Fe_3O_4 deduced from the spectra in (a). Note the strong MCD signals for weak features A and B.

field strength of 0.5 T. No magnetic-field dependence was seen in the MCD signal for the field change from 0.5 to 1.5 T. Two weak features in the prethreshold region are labeled A and B. The main peak at the $M_{2,3}$ edges exhibits a large negative MCD signal, which is similar to the behavior in Ni. However, the overall structure in the MCD spectrum is much more complicated than that for Ni. The most interesting is an anomalously strong MCD signal observed for the very weak multiplet structures (A and B). This is the first observation of MCD in the core-edge prethreshold region to the best of our knowledge.

A comparison of the present reflectance spectra with the absorption spectra of Fujimori *et al.*[22] for Fe_xO and Fe_2O_3 indicates that features A and B might be identified as arising from intra-atomic transitions in Fe^{2+} and Fe^{3+} ions, respectively, on the assumption that no appreciable energy shifts occur for different oxides. In spinel-type ferrimagnetic Fe_3O_4, the spin magnetic moments of the Fe^{3+} ions on the oxygen-tetrahedrally coordinated ($8a$) sites and the octahedral ($16d$) sites are canceled out and only the Fe^{2+} ions on the octahedral sites are responsible for the net magnetic moments. Hence, the MCD signals observed for feature A, as well as for the main $M_{2,3}$ peak, could be reasonably attributed to the remaining magnetic moments of the Fe^{2+} ions. However, a simple picture based on the above-mentioned assignment of B leads to difficulty in that its strong MCD seems to conflict with no net spin magnetic moments of the Fe^{3+} ions. A reasonable interpretation of the overall MCD spectrum of Fe_3O_4 requires detailed theoretical analyses of the origin of the multiplets.

In summary, we have observed MCD at and around the $M_{2,3}$ edges in single crystals of Ni and Fe_3O_4. The MCD spectrum of Ni could be well understood by the recent calculation by Yoshida and Jo,[21] which includes the contribution of the orbital magnetic moment. The strong MCD of the prethreshold multiplets in Fe_3O_4 suggests that the $M_{2,3}$ MCD experiments combined with proper theoretical model calculations would provide a sensitive probe of the local magnetic states of magnetic $3d$-electron systems.

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