X-Ray Magnetic Dichroism of Antiferromagnet Fe_2O_3: The Orientation of Magnetic Moments Observed by Fe $2p$ X-Ray Absorption Spectroscopy

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We report strong magnetic linear dichroism at the Fe $L_{2,3}$ edge of the antiferromagnet Fe_2O_3 (hematite). The relative difference in absorption for light polarized parallel and perpendicular to the magnetic moment is as high as 40% at the Fe L_2 edge. The spectra are in excellent agreement with calculations of magnetic dichroism for Fe^{3+} ($3d^5$). The magnetic origin of this dichroism is demonstrated by the Morin transition at $\approx -10\,^\circ C$, where the moments in Fe_2O_3 rotate by 90°. Magnetic linear dichroism may be applied to measure the spin orientation in thin films and multilayers, and to image magnetic domains.

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Since the prediction [1] and observation [2] of strong magnetic linear dichroism at the $M_{4,5}$ edges in rare earths, x-ray magnetic dichroism has received great interest. However, attention has focused on x-ray magnetic circular dichroism (XMCD), the difference in absorption cross section for right- and left-circular polarization. XMCD is valuable in the study of ferromagnetic materials [3-5], but XMCD requires a net magnetization since it is proportional to the expectation value of the local magnetic moment $\langle M \rangle$. Therefore XMCD is absent in the extensive group of antiferromagnetic materials. But magnetic linear dichroism is just as strong in antiferromagnets as in ferromagnets. X-ray magnetic linear dichroism (XMLD) is the difference in cross section for light polarized perpendicular or parallel to the magnetic moment, and it depends on $\langle M^2 \rangle$ of the ions [1]. XMLD can therefore be strong in any system with collinear magnetic ordering, whether it be ferromagnetic or antiferromagnetic. Recent calculations by van der Laan and Thole [6] predict strong magnetic linear dichroism at $L_{2,3}$ edges of $3d$ transition metals, on the order of 20%.

Magnetic linear dichroism is also observed using visible light (e.g., in $KNiF_3$ [7]), but its uncertain sign at the forbidden d-d transitions [8] precludes determination of a spin orientation. XMLD on the other hand can determine the orientation of magnetic moments absolutely. This method supplements neutron diffraction, because it does not require a large volume of material. Although XMLD cannot give details of the magnetic structure, it has the advantage of not depending on magnetic ordering. For instance, XMLD could determine the orientation of the moment on impurities. It is a local, element-specific probe of the magnetic moment, like Mössbauer spectroscopy, NMR, and other hyperfine measurements. Magnetic dichroism has all the versatility of x-ray absorption spectroscopy: One can study bulk spectra by measuring the fluorescence of the core hole (sampling several thousand angstrom) or just the first few atomic layers by measuring the intensity of Auger electrons. This makes magnetic dichroism especially suitable for studying magnetism of surfaces and thin films.

However, the potential usefulness of XMLD is compromised by the fact that linear dichroism is not only caused by magnetism, but also by axial components of the crystal field. While the magnetic origin of circular dichroism in a ferromagnet can be easily proven by reversing the magnetization direction, experimental proof of the magnetic origin of linear dichroism requires rotation of the spin orientation without turning the crystal, which is often difficult because of magnetocrystalline anisotropy. Indeed, in a recent study the linear dichroism of dysprosium on silicon was explained by an axial crystal field, although the measured dichroism agreed with the shape (but not the magnitude) of the calculated Dy $3d^{10}4f^9 \rightarrow 3d^9 4f^{10}$ magnetic linear dichroism [9,10]. To dispel a possible impression that the attribution of linear dichroism to magnetic effects would be rather doubtful in general, we show in this paper linear dichroism spectra that are unambiguously magnetic in origin. In Fe_2O_3 we have found a model system which provides the first clear evidence for magnetic linear dichroism in an antiferromagnet [11]. We observe that the dichroism spectrum agrees with the calculations both in shape and magnitude. Furthermore, in Fe_2O_3 we can rotate the spin orientation by just changing the temperature while keeping the crystal in place, thus checking the magnetic origin of the dichroism experimentally.

Hematite (α-Fe_2O_3) [12] has an interesting magnetic phase transition at $\approx -10\,^\circ C$ (first discovered by Morin [13]), in which the angle between the direction of the magnetic moments and the c axis of the crystal changes by 90°. The antiferromagnetic ordering does not change at this phase transition: Neutron diffraction studies of the spin structure [14,15] have shown that the moments are always parallel within any basal plane, neighboring planes being antiferromagnetically coupled. But at low temperatures the spins are aligned parallel to the trigonal c axis (perpendicular to the basal plane), while above the Morin temperature ($\approx -10\,^\circ\mathrm{C}$) the moments are rotated by 90°, perpendicular to the c axis. The high-temperature phase with moments parallel to the basal plane has three magnetic domains with spin orientation differing by 120°. The Morin transition has also been studied by the Mössbauer effect [16], by linear magnetic birefringence [17], and by magnetic x-ray diffraction [18,19]. Hematite has the uniaxial corundum Al_2O_3 crystal structure in which the iron atoms are coordinated by six oxygen atoms with slight deviations from octahedral (O_h) symmetry. As no significant structural modification has been noted at T_M ($\approx -10\,^\circ\mathrm{C}$) [12], we expect to observe changes in the absorption spectrum due to the change of spin direction directly, without disturbing effects from structural anisotropy.

The experiments were carried out at the AT&T Bell Laboratories Dragon beam line [20] at the National Synchrotron Light Source. The photon energy resolution was set at 0.2 eV and the degree of linear polarization was 98% at the Fe L_3 edge. The absorption was detected by measuring the total electron yield, which probes a ~100 Å thick layer.

The measurements were done on synthetic crystals of Fe_2O_3, grown by J. P. Remeika (AT&T Bell Laboratories). The data shown in this paper refer to a sample which consisted of a column of rhombohedra, stacked along the c axis. This column was held perpendicular to the beam. In the horizontal orientation one measures spectra with light polarized parallel to the c axis. By turning the column vertically, one measures spectra with the polarization perpendicular to c, using the same angle of incidence on the same surface of the crystal.

We calculated the $L_{2,3}$ absorption spectra for different polarization directions using the methods described by van der Laan and Thole [6]. First an atomic Hartree-Fock calculation gives the spin-orbit interaction of the $2p$ core hole that splits the L_2 ($2p_{1/2}$) and L_3 ($2p_{3/2}$) edges, and the p-d and d-d Coulomb and exchange interactions that cause multiplet structure within the edges. Calculating the atomic $2p$ absorption spectrum involves the calculation of reduced matrix elements for the initial ($3d^5$) and final ($2p^5 3d^6$) configurations in spherical symmetry. But because the ligand field splitting of $3d$ transition metals is of the same order of magnitude as p-d and d-d interactions (1–2 eV), a crystal field has to be taken into account. In an octahedral lattice position this requires one parameter, $10Dq$, the difference in energy between e_g ($x^2-y^2, 3z^2-r^2$) and t_{2g} (xy,yz,xz) orbitals. In order to get a polarization dependence, one needs to break the octahedral symmetry of the ground state by a spin operator which simulates the alignment of the magnetic moments. With the spin aligned along a trigonal axis of the crystal field, the symmetry is reduced to C_{3i}. Because the superexchange interaction is an order of magnitude smaller than the crystal field, it is treated as a perturbation, using the Wigner-Eckart theorem to calculate C_{3i} eigenstates. In C_{3i} the electric dipole operator is split into terms representing z, left-, and right-circular polarization. The z term gives the intensity for the electric vector parallel to the magnetic axis, and the sum of the left and right terms gives the intensity perpendicular to the axis. The calculated spectrum is created by applying a Lorentzian to the lines to represent lifetime broadening, and then by convoluting with a Gaussian to simulate the instrumental resolution.

Figure 1 shows the Fe $L_{2,3}$ absorption spectrum of powdered Fe_2O_3. The powder spectrum is the same at room temperature and after cooling below the Morin transition. Also shown is the calculated isotropic $2p^6 3d^5 \rightarrow 2p^5 3d^6$ spectrum for Fe^{3+} for an octahedral crystal field. As usual, the effects of covalency were simulated by reducing the d-d direct Coulomb and exchange parameters to 70% of the Hartree-Fock values, and the p-d direct Coulomb parameter to 80% [21]. The value of $10Dq = 1.45$ eV for the crystal field gave the best fit to the experimental spectrum. The peaks at the L_3 and L_2 edges were broadened by Lorentzians of different widths. At the L_3 edge the first peak was broadened by 0.1 eV, and the rest by 0.3 eV; at the L_2 edge the first peak was broadened by 0.45 eV and the rest by 1.0 eV. While the larger width of the L_2 edge is due to Coster-Kronig decay of the $2p_{1/2}$ core hole, our use of different Lorentzian broadenings within the L_2 and L_3 edges is not more than a fit; it may be due to a combination of lifetime and phonon effects [22]. The spectrum was convoluted with a Gaussian (FWHM = 0.25 eV) to simulate the resolution function.

We observe that there is very good agreement between

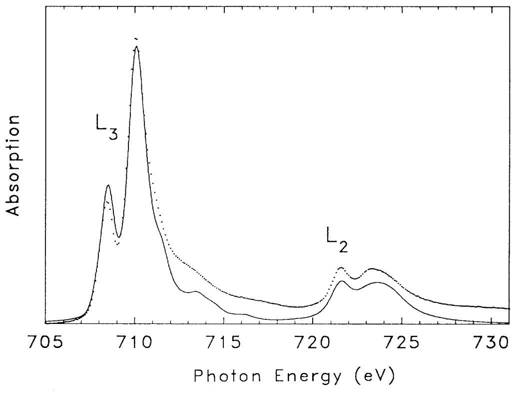

FIG. 1. Comparison of the Fe $2p$ absorption spectrum of Fe_2O_3 powder (points) with a calculation for Fe^{3+} ($3d^5$) in octahedral symmetry (line).

experiment and calculation. This indicates that the deviation of the crystal field from octahedral symmetry is not very important. The measured absorption around 718 eV is stronger than calculated because transitions to $2p^5 3d^7 \underline{L}$ states ($\underline{L}$ denotes a ligand hole) have not been considered in the calculations [21].

Next we turn to the linear dichroism. Figure 2 shows data taken at 80 K. There is a strong orientation dependence of the absorption spectrum, most clearly in the shape of the L_2 edge. In the same figure we show the calculated spectra for polarizations parallel (top) and perpendicular (bottom) to the magnetic moment, so that the theoretical spectra correspond to the known moment directions ($\mathbf{M}\parallel c$). In the calculation we used the same parameters that were used for fitting the isotropic spectrum. The only extra parameter is the 0.03 eV splitting of the magnetic sublevels; for this value the occupation of thermally excited states is hardly noticeable at room temperature. We see that there is good agreement between the observed and the calculated spectra. The calculated magnetic dichroism accounts for the experimental differences between the two polarization directions.

Figure 3 shows two spectra that demonstrate the magnetic origin of the dichroism in Fe_2O_3. Both spectra were taken with $\mathbf{E}\parallel c$, only the temperature is different. The dashes represent measurements at room temperature (above the Morin transition, $\mathbf{M}\perp c$), the line shows measurements at 200 K (below the Morin transition, $\mathbf{M}\parallel c$). The spectra were scaled on the background. The vertical scale is chosen so that the maximum isotropic Fe absorption is 100% over the background. The spin-flip transition induces strong changes in the absorption spectrum. The room-temperature $\mathbf{E}\parallel c$ spectrum is very similar to the low-temperature $\mathbf{E}\perp c$ spectrum of Fig. 2. Although the polarization with respect to the crystal field is different in these two cases, in both cases the polarization vector is perpendicular to the moment, and both spectra are in good agreement with the calculations for $\mathbf{E}\perp\mathbf{M}$. This example shows that magnetic effects can dominate linear dichroism, even if the crystal field has an axial component.

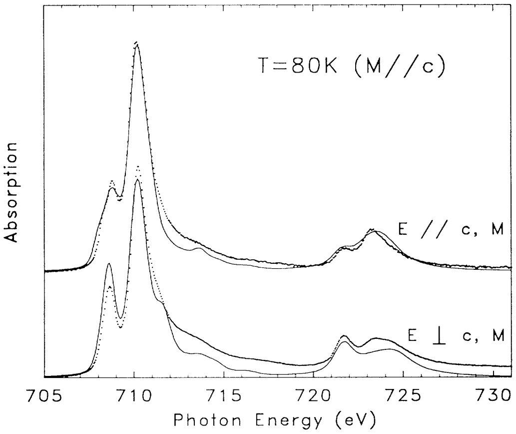

FIG. 2. Fe $2p$ XAS of Fe_2O_3 for two orientations of the crystal at 80 K (points). The lines are calculations for x-ray polarization parallel and perpendicular to the magnetic moment.

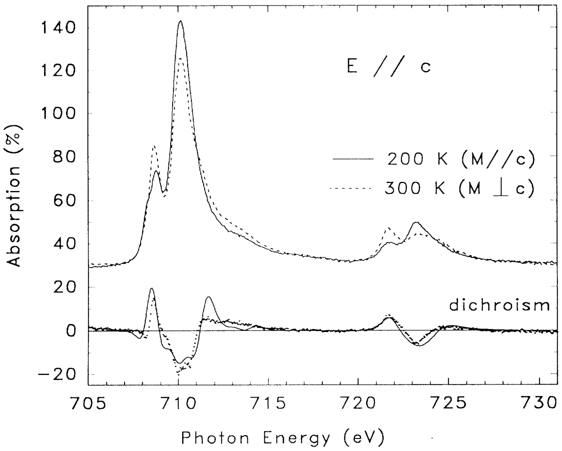

FIG. 3. Fe $2p$ XAS of Fe_2O_3 with **E** parallel to the c axis, at room temperature (dashed line) and below the Morin transition (solid line). On the same scale the difference (points) is compared to the theoretical magnetic linear dichroism (solid line).

To bring out the dichroism more clearly, we also show in Fig. 3 the difference spectrum of the 200 and 300 K spectra. The integrals of the difference spectrum over each of the L_3 and L_2 edges are zero within experimental accuracy. The strongest peaks in the difference spectrum are about 20% of the maximum absorption. The calculated linear dichroism is also shown in Fig. 3. It matches very well with many features in the experimental difference spectrum. The relative strength of the experimental and the calculated dichroism was determined by scaling the experimental and theoretical $\mathbf{E}\parallel\mathbf{M}$ spectra. The fact that the magnitude of the experimental dichroism agrees with the theoretical prediction shows that the magnetic ordering in the surface layer ($\sim$100 Å) is essentially complete.

What is the physics behind these large magnetic effects? The origin of magnetic linear dichroism observed here lies in the broken symmetry of light with polarization **E** parallel or perpendicular to the magnetic moment **M**. The direct magnetic interaction of electromagnetic interaction with the spin of the electrons is undetectably small at this edge. Therefore we discuss only electric dipole transitions, where the connection between magnetism and polarization is indirect, mediated by the spin-orbit coupling. Spin polarization of the $3d$ orbitals and the well separated spin-orbit splitting of $2p_{1/2}$ and $2p_{3/2}$ core hole states are the essential ingredients of strong circular dichroism in ferromagnets [3]. But if only spin-orbit interaction of the core hole is considered, the average of spectra taken with left- and right-circular polarization is equal to the isotropic spectrum, so that there is no linear dichroism. Strong linear magnetic dichroism appears when multiplet structure within the L_2 or L_3 edges can be observed. Part of the multiplet structure is due to the splitting of final states with different total (spin+orbital) angular momentum. The selection rule for angular momentum is $\Delta J = -1,0,1$. The different selection rules for polarization parallel to the moment ($\Delta m = 0$) and perpendicular to the moment ($\Delta m = \pm 1$) make transitions to final states with $J' = J-1, J, J+1$ have different intensities.

To show that the $\Delta m = 0$ ($\mathbf{E} \parallel \mathbf{M}$) spectrum is not just the average of the $\Delta = \pm 1$ spectra, we will treat Fe^{3+} in some detail. Magnetic dichroism of free Fe^{3+} is relatively simple, because iron is in a high spin $3d^5$ state with no orbital angular momentum. The atomic ground state is $^6S_{5/2}(L=0,\, S=\frac{5}{2},\, J=\frac{5}{2})$. In a magnetic field H the degenerate ground state is split into six Zeeman levels with quantum numbers $m_J = -\frac{5}{2}, -\frac{3}{2}, \ldots, \frac{5}{2}$. At $T=0$ only the ground-state level $m_J = -\frac{5}{2}$ is occupied. In the final state J' is a good quantum number due to the large core hole spin-orbit interaction of 13 eV. The selection rule $\Delta J = +1, 0, -1$ permits transitions to $J' = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}$. Then the selection rule $\Delta m = 0$ for radiation linearly polarized along the direction of the magnetic moment allows transitions to $J' = \frac{7}{2}$ and $\frac{5}{2}$, but not to $J' = \frac{3}{2}$ levels, since only $J' = \frac{7}{2}$ and $\frac{5}{2}$ have $m_J = -\frac{5}{2}$ sublevels. Thus the $J' = \frac{3}{2}$ final states that are allowed by $\Delta m = -1$ in the $\mathbf{E} \perp \mathbf{M}$ spectrum are absent in the $\mathbf{E} \parallel \mathbf{M}$ spectrum.

It has been noted that the ground state can be split by an axial crystal field in sublevels which are paired with opposite m_J values (e.g., $\pm\frac{5}{2}, \pm\frac{3}{2}, \pm\frac{1}{2}$) [9]. This leads to dichroism spectra similar in shape to magnetic dichroism spectra. However, this crystal-field-induced dichroism is smaller than magnetic dichroism, because an electric field gradient leaves positive and negative m_J levels degenerate [10]. It is therefore important to note that also the magnitude of the dichroism in $\mathrm{Fe_2O_3}$ agrees with the calculated magnetic linear dichroism.

We have shown by measurements of the Fe $2p$ x-ray absorption spectra of $\mathrm{Fe_2O_3}$ that x-ray magnetic linear dichroism can be strong in antiferromagnets. Calculations for an Fe^{3+} ($3d^5$) ion in an octahedral crystal field are in excellent agreement with the spectra measured with polarization directions parallel and perpendicular to the magnetic moment. The reversal of the dichroism at $\approx -10\,^\circ\mathrm{C}$ caused by the spin-flip transition (Morin transition) in $\mathrm{Fe_2O_3}$ convincingly shows that the observed dichroism is indeed related to the orientation of the magnetic moment. The magnitude of the changes is as high as predicted by the calculations: about 20% at the strongest absorption peak in the L_3 edge. Magnetic dichroism gives important additional spectroscopic information about the electronic structure. In conjunction with calculations, XMLD is a unique tool for measuring the orientation of the magnetic axis in both ferromagnets and antiferromagnets, especially useful for thin films and surfaces. With an x-ray microscope, one could image antiferromagnetic domains.

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