

## Resonant X-Ray Diffraction near the Iron $K$ Edge in Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>)

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An unexpected resonant enhancement in x-ray diffraction occurs at a forbidden reflection in the antiferromagnet hematite. This fiftyfold increase in the diffracted signal, 10 eV below the iron  $K$  edge, exhibits a rotation in the x-ray polarization and a 60° azimuthal symmetry as the crystal is rotated about the reflection vector. The effect is explained to result from *electronic quadrupole transitions* in the anomalous scattering from iron and demonstrates that diffraction can be a sensitive probe of the electronic environment at specific atomic sites in the crystal.

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Recently, the scattering of x rays at or near an absorption edge in atoms and nuclei has revealed a rich variety of phenomena which are of fundamental interest and useful application. One example, the phenomenon of anisotropy of anomalous dispersion (AAD), can arise in the diffraction of x rays when the resonating atoms exist in an anisotropic crystalline environment [1]. The effect results from the influence of electronic transitions associated with the edge, which in turn depend on the spatial distribution of empty electronic levels of the atom. In essence, the local symmetry can distort the wave functions of outer electrons, and thus the atomic scattering factor will no longer be a scalar and the diffraction may exhibit birefringence. In addition, when these atoms occur with more than one molecular orientation, forbidden reflections [2,3] may become observable.

This paper presents experimental evidence for a novel kind of anisotropic x-ray scattering near the  $K$  edge in iron. We have observed diffraction which results from differences in the *electric quadrupole* contribution to scattering from iron atoms at a reflection that is forbidden by the rules of the space group *and* by current models of anisotropic scattering. In hematite, this resonant diffraction exhibits a rotation of the x-ray polarization and a dependence on angle consistent with crystal-field-induced distortions of the iron  $3d$  shell caused by the octahedral arrangement of nearest-neighbor oxygen atoms. These results demonstrate that x-ray diffraction can associate a particular feature in a near-edge absorption spectrum with differences in the environment at symmetry-related sites of the absorbing species.

Hematite has the space group  $R\bar{3}c$  [4] with two molecules in the rhombohedral primitive cell. The iron atoms lie along the trigonal  $c$  axis, slightly offset from the center of octahedra formed from triangles of oxygen lying parallel to the basal plane. The glide planes which intercept the threefold axis imply, for octahedra separated by  $c/6$ , a rotation of 180°. We have studied diffraction at the rhombohedral (111) reflection (diffraction planes separated by  $c/3$ ) which is forbidden because of the glide-plane symmetry.

An interesting experimental complication arises for this reflection because the iron atoms are magnetic and form

an antiferromagnetic arrangement which permits magnetic x-ray scattering [5]. We compare the strength of the electronic resonance scattering to this magnetic scattering, and in addition we show that the two effects can be distinguished by studying a magnetic phase transition.

The theory that describes our findings has been worked out by Hamrick, Hannon, and Trammell [6], and will be presented elsewhere. The essential experimental results can be understood by considering the amplitude for scattering of a photon of energy  $\hbar\omega_k$ , in second-order perturbation theory [7]:

$$A \sim \sum_c \frac{\langle a | \boldsymbol{\varepsilon}' \cdot \mathbf{r} (1 - i\mathbf{k}' \cdot \mathbf{r}) | c \rangle \langle c | \boldsymbol{\varepsilon} \cdot \mathbf{r} (1 + i\mathbf{k} \cdot \mathbf{r}) | a \rangle}{E_a - E_c + \hbar\omega_k + i\Gamma_c/2}.$$

This expression gives the amplitude contributed to Bragg scattering by a transition from a ground state  $|a\rangle$  of energy  $E_a$  involving a single electron of the absorbing atom. The sum is over the allowed intermediate states  $|c\rangle$  of the transition with energy  $E_c$  and width  $\Gamma_c$ . A second sum, over atom positions, is required to calculate a structure factor for the reflection. The factors that involve scattering geometry are displayed in the inset of Fig. 2. The *dipole* (first) term in this expansion is equivalent to the approximation used in current models describing AAD [3,8,9]. For transitions from the spherical  $K$  shell, these integrals measure the oddness (*first moment*) of the intermediate state along the polarization directions. The *quadrupole* (second) term is quadratic in the position coordinates and therefore is sensitive to the *second moment* of the intermediate-state wave functions.

In hematite, the Fe<sup>3+</sup> ion has a half-filled  $3d$  shell and if we approximate the electronic environment as purely octahedral [10], the crystalline electric field will split the  $3d$  orbitals into bonding ( $e$ ) and antibonding ( $t_2$ ) states [11] of slightly different energy. Both states display threefold symmetry about the  $c$  axis, with the  $e$  ( $t_2$ ) states directed toward (between) the near-neighbor oxygen atoms. At any one site, interference between transitions to these states of different energy and orientation results in a threefold variation in scattering amplitude (sixfold in intensity) as the crystal is rotated about the  $c$  axis. The orientation in space of these wave functions follows

the octahedra and is rotated by  $180^\circ$  about the  $c$  axis for iron sites separated by  $c/6$ . This difference in orientation reverses the phase (for some amplitude terms) of the quadrupole scattering from these two sites producing a nonzero intensity for the (111) reflection. Finally, for  $c$ -axis reflections, it is easily shown that the quadrupole scattering couples states of orthogonal polarization leading to a rotation in the x-ray polarization.

The experiments were performed at the CHESS F2 station with the beam from a 25-pole wiggler, focused by a sagittal-focusing double-crystal silicon (111) monochromator. At the iron  $K$  edge, 7.112 keV, the energy resolution is 2 eV and the flux at the sample exceeds  $10^{11}$  photons/s. The higher-order reflections in hematite are suppressed by use of a total reflection mirror that reduces harmonic contamination in the incident beam by 4–5 orders of magnitude and by energy discrimination of signals from a sodium iodide detector. The beam size is defined by slits positioned downstream of the mirror, just before the nitrogen monitor chamber and sample. The hematite is a natural crystal with the surface cut normal to the  $c$  axis.

The inset in Fig. 2(a) shows the scattering geometry and illustrates how azimuthal scans, where the crystal is rotated about the axis of the reflection vector, were made. In order to maintain the Bragg condition during these scans, the hematite  $c$  axis was aligned parallel to the  $\phi$  axis of the four-circle diffractometer. A Bragg diffraction polarization analyzer [12] using a perfect silicon (331) reflection with a  $44.4^\circ$  Bragg angle at the iron edge is mounted on the detector arm. The analyzer further acts to suppress fluorescence at the diffraction detector. The incident beam polarization was measured several times during these experiments and found to be 93% linearly polarized parallel to the plane of the storage ring. The measurements performed at low temperature use a Displex closed-cycle helium refrigerator and cold finger equipped with a specially built copper double-cradle goniometer that maintains accurate crystal alignment with changes in temperature.

Figure 1 displays the measured energy dependence of the hematite (111) reflection in a region just below the iron  $K$  edge. The integrated intensity is obtained by rocking the hematite through the reflection with the analyzer set for a maximum reflectivity. The open (solid) circles represent the  $\sigma$  ( $\pi$ ) component of polarization analyzed in the scattered beam. The  $\phi$  angle is  $-9.79^\circ$ , with zero corresponding to an oxygen atom lying in the scattering plane. The inset shows the absorption coefficient ( $\mu$ ) determined [13] by monitoring the sample fluorescence with a detector viewing the sample at  $90^\circ$  to the incident beam. The results are consistent with those found in Ref. [10]. The diffraction data are multiplied by  $\mu$  to correct for absorption in the sample. Another correction (not made) is to scale the  $\pi$  curve by 5 to account for throughput of the analyzer. A sharp increase in  $\pi$

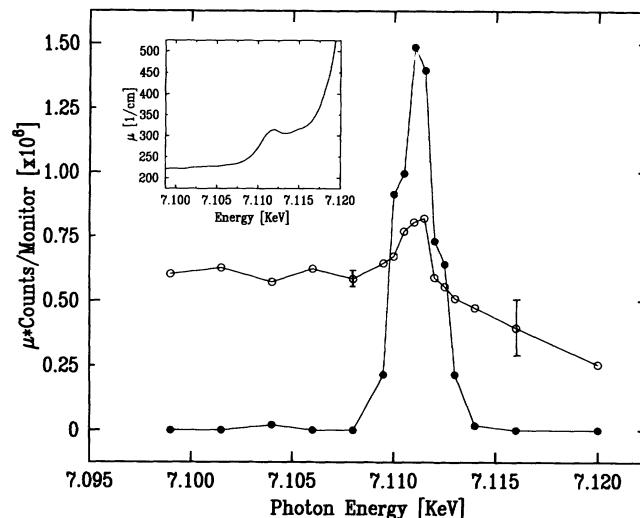


FIG. 1. Resonant behavior of the integrated intensity in single-crystal  $\alpha$ - $\text{Fe}_2\text{O}_3$  as a function of energy. The linear polarization diffracted at the rhombohedral (111) reflection has been analyzed; solid (open) circles represent the  $\pi$  ( $\sigma$ ) component of polarization. The intensity is scaled to account for absorption as the x-ray energy approaches the iron  $K$  edge. Inset: The absorption coefficient determined (see text) from fluorescence.

scattering is found at 7.111 keV or about 1 eV below the maximum in the absorption signal. The peak width matches the 2 eV energy width expected from the monochromator. The  $\sigma$  scattering undergoes a small increase above a base line signal visible at lower energies. No further resonance behavior was observed at energies up to the inflection point in the main absorption spectrum.

In Fig. 2 the azimuthal ( $\phi$  angle) dependence of the  $\sigma$  and  $\pi$  scattering for this (111) reflection is shown at several different energies. The data were collected by maximizing the diffraction from the hematite after each  $\phi$  step while the analyzer was set for maximum throughput. The flat response in  $\sigma$  scattering at 7 keV is expected from nonresonant magnetic scattering in an unmagnetized crystal which has trigonal magnetic domains of equal population. A sixfold intensity pattern emerges for both scattered polarization components when the energy is tuned near the resonance. The  $\pi$  and  $\sigma$  scattering track together in angle, but at resonance, with analyzer throughput considered, the peak in  $\pi$  is about 10 times the peak in  $\sigma$  and some 40 times larger than the  $\sigma$  scattering minimum. A characteristic feature is that the  $\pi$  intensity drops to zero at this angular minimum while the sixfold pattern of  $\sigma$  scattering appears to be added on top of the nonresonant signal. As a function of azimuthal angle, the resonant scattering minima correspond to an oxygen atom lying in the scattering plane. Hematite displays multiple beam or Renninger reflections [14] which have been deleted in presenting these scans.

Figure 3 shows that the base line scattering, attribut-

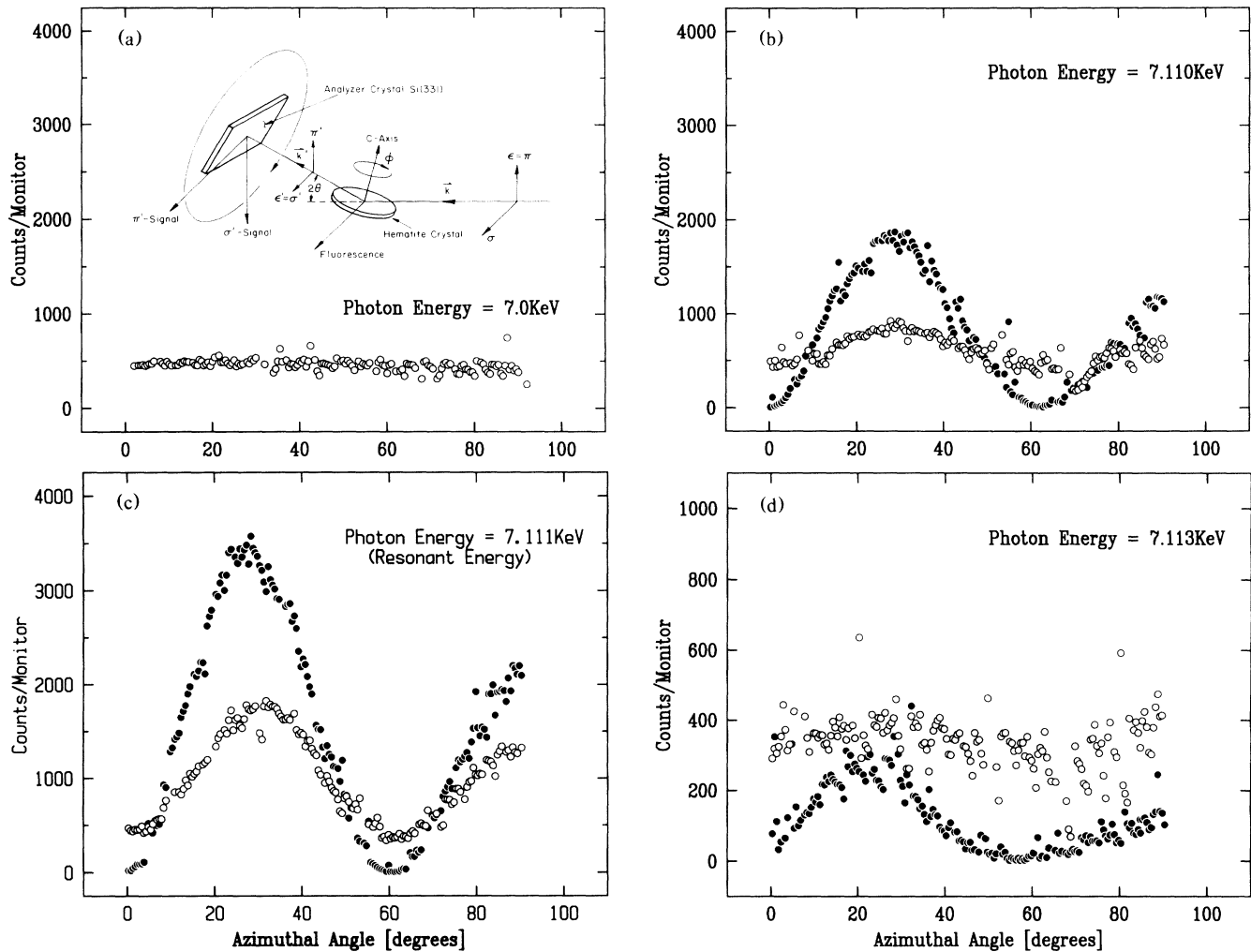


FIG. 2. Peak diffracted intensity of the (111) reflection when the hematite crystal is rotated about the reflection vector. Solid (open) circles display  $\pi$  ( $\sigma$ ) polarization in the diffracted beam for incident energies of 7.0, 7.110, 7.111 (resonance), and 7.113 keV. The experimental uncertainty is statistical; Renninger reflections (see text) are removed from the data. A  $60^\circ$  symmetry is expected from electric transitions in iron. Inset to (a): Schematic of the scattering experiment and definition of symbols in the equation.

ed to magnetic scattering, can be separated from the electronic resonance signal. Below about 260 K the magnetic moments turn out of the basal plane to point along the  $c$  axis; this is the so-called Morin transition [15]. The open points are azimuthal scans performed on the resonant energy measured at 200 and 220 K. The solid points were obtained at room temperature (291 K) under the same conditions as the low-temperature data. The magnetic signal is proportional to the component of the spin normal to the scattering plane and should be suppressed below the transition temperature. Indeed we observe that the base line scattering has dropped away with no significant change in the amplitude of the sixfold oscillation pattern. These results indicate that the resonance signal is not the result of magnetic scattering, including the electric dipole transitions of resonant exchange scattering [16].

To more accurately compare the strengths of resonant

and nonresonant scattering we have measured the analyzer crystal integrated intensity with the hematite at the peak in the (111) reflection. The measurements are performed at room temperature, using an unmagnetized crystal positioned at the peak in the sixfold pattern ( $\phi = 30.36^\circ$ ) and are corrected for energy-dependent absorption. Relative to unit scattering off resonance (7.06 keV), the resonant  $\sigma$  intensity (after subtracting the non-resonant base line) is  $3.5 \pm 0.5$  and the  $\pi$  intensity is  $48.0 \pm 5.0$ . The ratio of resonant  $\sigma$  to  $\pi$  intensity is consistent with the measured degree of polarization in the incident beam and the prediction that the scattering produces a  $90^\circ$  rotation of this polarization.

In conclusion, we have observed a resonance in diffraction from hematite just below the iron  $K$  edge. This reflection should not occur for x rays scattering from electron charge unless one considers a new mechanism,

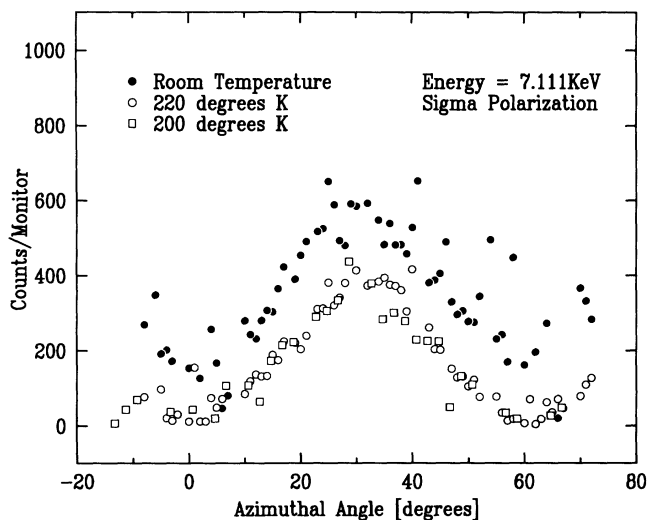


FIG. 3. Temperature dependence of resonant ( $\sigma$ -polarization) diffraction at 291, 220, and 200 K. The sixfold pattern at 291 K sits atop a base line which disappears at low temperature. At about 260 K the magnetic moments in hematite rotate out of the basal plane to point along the  $c$  axis. These data suggest that the resonant effect is not the result of magnetic scattering.

quadrupole anomalous diffraction. These results have motivated a new theoretical understanding of resonant x-ray scattering with some interesting applications in the study of electronic structure. X-ray-absorption near-edge spectroscopy (XANES) averages the influence of the electronic environment at absorbing atoms. As illustrated in this work, the study of near-edge spectra using diffraction can provide information on differences in coordination at symmetry-related sites. By a judicious choice of reflections, resonant diffraction should help to connect near-edge features with symmetry-inequivalent sites. Further, as compared to XANES, the study of forbidden reflections and the use of polarization analysis offers a great improvement in the signal-to-noise ratio. Because of its sensitivity, this novel form of resonant scattering may provide information about solid-state perturbations of electronic structure which depend, for example, on changes in thermodynamic variables.

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