

Polarized Dispersion of X-rays in Pyrite

DAVID H. TEMPLETON* AND LIESELOTTE K. TEMPLETON

Department of Chemistry, University of California, Berkeley, CA 94720, USA. E-mail: lilo@lbl.gov

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Abstract

Diffraction of synchrotron radiation in a crystal of FeS_2 reveals dipolar anisotropy of anomalous scattering by Fe near its K -absorption edge, in spite of the almost-regular octahedral geometry of the nearest S neighbors. At 7121 eV, the magnitude of f changes with polarization direction by as much as 0.7 electron units. No effects of quadrupolar anisotropy were detected.

1. Introduction

The complex amplitude $f_0 + f' + if''$ that represents magnitude and phase for elastic scattering of X-rays by an atom is usually assumed to be a scalar that depends on polarization by a factor that is the same for all atoms. In many materials, the anisotropy of atomic environment and chemical bonding is sufficient, for wavelengths near absorption edges, to give rise to significant dichroism, birefringence and anisotropic dispersion. Then tensors are needed to describe the scattering (Templeton & Templeton, hereafter T&T, 1982; Dmitrienko, 1983; Belyakov & Dmitrienko, 1989; Brouder, 1990; Blume, 1994). These tensors cause f to change with polarization state and with molecular orientation so that 'equivalent' atoms may have different scattering amplitudes, 'forbidden' reflections may be observed and new methods for finding phases of structure factors are possible (*e.g.* T&T, 1991; Kirfel & Petcov, 1992). Tensors of second rank, which correspond to dipole resonances and neglect the finite size of the atom, have been sufficient in most cases until now. A mixed dipole–quadrupole resonant scattering term can require a tensor of third rank for atoms in sites that lack inversion symmetry (T&T, 1994). Tensors of fourth rank are needed for quadrupole scattering like that observed by Finkelstein, Shen & Shastri (1992) in hematite (Fe_2O_3). The tensors of rank higher than two contain the dependence of f on Bragg angle, other than that given by the conventional polarization factor $\mathbf{e} \cdot \mathbf{e}'$.

In search of another example of fourth-rank-tensor effects, we studied scattering by a crystal of pyrite (FeS_2) near the Fe K -absorption edge. The absorption spectrum (Fig. 1) shows resonances at 7113 and 7121 eV. The cubic crystal structure of pyrite tends to obscure anisotropy of absorption but can be an advantage for measurement of the anisotropy of

scattering. We expected that dipole effects would be nearly isotropic because of the nearly regular octahedral environment of the Fe atom. Significant anisotropy was discovered. Its variation with azimuth corresponds to a second-rank tensor and could not be explained by a tensor of fourth rank.

2. Structure of pyrite

Pyrite is cubic, $c2$ -type, space group $Pa\bar{3}$ [formerly designated $Pa3$] (Bragg, 1914; Ewald & Friedrich, 1914), $a = 5.417 \text{ \AA}$ (Swanson, Gilfrich & Ugrinic, 1955). Fe atoms are in sites $4(a)$ 0,0,0 *etc.* and S atoms in $8(c)$ x, x, x *etc.*, $x = 0.384$ (Elliott, 1960) or 0.3851 (Finklea, Cathey & Amma, 1976). Pyrite crystals can be non-stoichiometric and cell dimensions vary slightly. A redetermination with the crystal used in this study gave $a = 5.415(1) \text{ \AA}$, $x = 0.3849(1)$, r.m.s. displacements = 0.088(1) \AA for Fe and 0.096(1) \AA for S with barely significant anisotropy. Finklea, Cathey & Amma (1976) reported 0.056 and 0.062 \AA for these displacements but with no mention of possible extinction effects, which, if uncorrected, tend to reduce them.

Each Fe atom (site symmetry $\bar{3}$) has six S atoms as nearest neighbors at the corners of a not-quite-regular

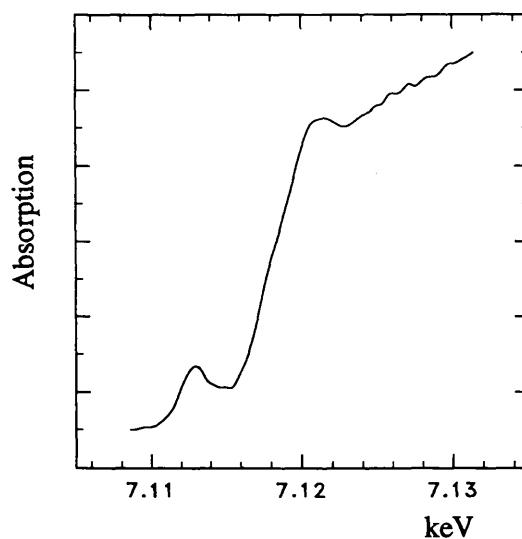


Fig. 1. X-ray absorption spectrum of pyrite at the Fe K edge.

octahedron [Fe—S = 2.264 (1) Å, S—Fe—S = 85.65 (1) and 94.35 (1)°]. These octahedra have four orientations, each with its exact threefold axis parallel with one of the cube diagonals. In each case, the larger S—Fe—S angles are those nearest this axis.

3. Optical model

Here we neglect all magnetic effects. When the resonant scattering (but not f_0) is derived using the dipole approximation, the atomic scattering factor (including the polarization factor) for a particular combination of polarization components can be expressed as

$$f(\mathbf{e}, \mathbf{e}') = \mathbf{e} \cdot \mathbf{e}' f_0 + \sum_{j,k} e_j e'_k D_{jk}, \quad (1)$$

where e_j and e'_k are components of the polarization unit vectors \mathbf{e} and \mathbf{e}' and D is a complex tensor of second rank. For the Fe atom at the unit-cell origin, the diagonal terms

$$D_{11} = D_{22} = D_{33} = f'(jj) + if''(jj) \quad (2)$$

are the same as the ordinary isotropic dispersion correction. The off-diagonal terms, which represent the anisotropy, are

$$D_{12} = D_{23} = D_{31} = D_{21} = D_{32} = D_{13} = f'(jk) + if''(jk). \quad (3)$$

The extremes of f are $D_{11} + 2D_{12}$ for [111] polarization and $D_{11} - D_{12}$ for directions perpendicular to this axis. Tensors for Fe at other sites are the same except for some changes of sign. These parameters are dimensionless but sometimes 'electron units per atom' is added to them.

Quadrupole and mixed dipole–octopole resonances introduce two tensors of fourth rank. The angular properties of f calculated from these terms can be quite complicated. The algebraic details are omitted because these terms were not detected here.

Structure-factor algebra is important in the design of experiments to find these small effects. F for Fe is $+4f$ if indices are all even or all odd. If indices are of mixed parity, $F(\text{Fe})$ is zero except for effects of anisotropy of electron density, thermal motion or resonant scattering. Only the resonant scattering can make F change with azimuth. Structure factors for S may be large or small with either sign for any type of index. The effects of anisotropic scattering are best observed in reflections that are weak but not too weak. Those due to tensors of second rank can be detected with mixed-index reflections if the S structure factor is small and they may obscure any effects of fourth-rank tensors that also are present. Only tensors of fourth or higher rank can modulate all-even or all-odd reflections but no such reflection is weak enough to be a very sensitive probe.

4. Experimental

An irregular triangular fragment ($0.15 \times 0.19 \times 0.20$ mm) broken from a natural crystal of pyrite was glued to the end of a glass fiber. Diffraction data were recorded using an Enraf–Nonius CAD-4 diffractometer (Phillips, Cerino & Hodgson, 1979) on Beam Line 1–5 at SSRL [bending magnet, 45–90 mA ring current at 3 GeV, unfocused double-crystal Si(111) monochromator]. The degree of linear polarization was 90% according to a test with the Borrmann effect in a Ge crystal (T&T, 1988a). Integrated intensities for ω scans were corrected for isotropic absorption by analytical integration using 14 faces and μ ranging from 464 to 1314 cm⁻¹. The corrections were unsatisfactory for reflections on some sides of the crystal. The data reported here are confined to reflections on the side containing the largest face and some of them with excessively high absorption corrections were rejected. Data were also deleted if too strong or too weak or if duplicate scans failed to check. Photon energies near the Fe K edge were calibrated according to 7.111 20 keV (Bearden, 1967) for the first inflection measured with an iron foil. They may be in error by as much as 0.6 eV because of a backlash problem. Other details were as described by T&T (1995).

For determining the parameters of the scattering tensor, sets of a few chosen reflections were measured at many azimuthal settings. For the crystal structure refinement, 60 (39 unique) reflections were measured at 1.7464 Å, each at two azimuthal settings. Some were rejected because the least-squares refinement indicated that their intensities were reduced 25–50% by extinction effects. An empirical extinction correction reduced the remaining structure factors by 11% or less. Scattering factors for neutral atoms were from *International Tables for X-ray Crystallography* (1974) with dispersion corrections from Cromer (1983). With 32 unique reflections, $R = 0.036$, $wR = 0.058$.

5. Results

Anisotropy of dispersion at the 7121 eV peak was first detected by an azimuthal modulation of intensity for reflection 432 (Fig. 2). The structure factor for this weak reflection contains a small contribution from S and none from the isotropic part of the Fe scattering factor. It is sensitive to the anisotropy of $f'(\text{Fe})$, which changes sign at the resonant energy and causes the reversal of the modulation. The effect of anisotropy of $f''(\text{Fe})$ is smaller but significant near the center of the resonance. The calculated curves in Fig. 2 are based on tensor components chosen by trial and error: $D_{12} = 0.12 + i0.12$ (top), $0.06 + i0.20$ (middle), $-0.10 + i0.16$ (bottom). Terms for all four polarization combinations are included but those due to the small

amount of \mathbf{p} component in the incident radiation are almost negligible.

The anisotropy was also detected at 7120.4 eV with two reflections forbidden by the glide-plane rule (Fig. 3). Only the magnitude of D_{12} is determined by data of this type. The intensities were scaled as $|F|^2$ by comparison with reflection 332. A least-squares adjustment (which neglected the imperfect polarization and omitted data that are obviously affected by the Renninger effect) gave $|D_{12}| = 0.19(2)$. If the 5% \mathbf{p} component is included in the calculation, this is increased to 0.20.

Values of the dispersion parameters derived by the method of least squares from five data sets at four photon energies are listed in Table 1.

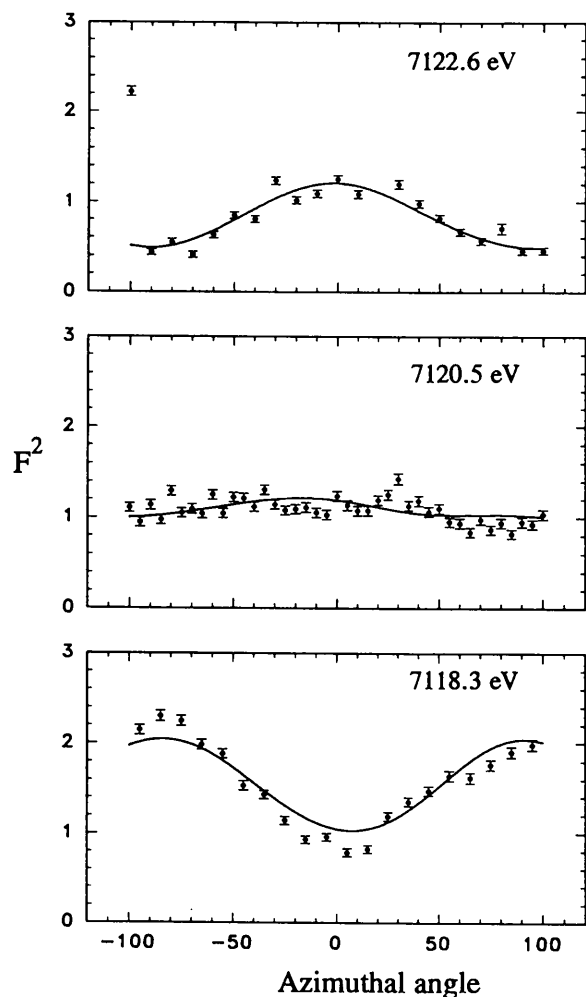


Fig. 2. Observed (points) and calculated (lines) change of intensity with azimuth for reflection 432 at three photon energies, showing reversal of modulation owing to sign change of $f'(jk)$. An outlier in the upper panel and several in Fig. 3 are the result of multiple reflection.

Table 1. Dispersion parameters from diffraction data

E (eV)	$f'(jj)$	$f''(jj)$	$f'(jk)$	$f''(jk)$	R (%)	n^*
7117.0	-8.70(6)	1.13(1)	0.02(1)	0.12(1)	5.0	527
7119.8	-8.65(8)	(3.2)†	-0.07(1)	0.19(1)	6.4	169
7121.1	-7.9(1)	3.5(1)	0.09(2)	0.29(6)	5.6	325
7121.1	-7.7(1)	3.5(1)	0.10(3)	0.15(10)	7.6	266
7122.4	-7.8(1)	3.2(1)	0.15(1)	0.12(2)	5.9	341

* Number of observations. † Assumed value, not refined.

6. Discussion

The anisotropy at the 7121 eV resonance ($|f_\sigma - f_\pi| \approx 0.7$) is less by an order of magnitude than that at K edges for some other atoms with less-symmetrical bonding (*e.g.* Se, T&T 1988*b*; Br, T&T 1995). Yet it is enough to cause substantial changes in the intensities of weak reflections. These results reflect the great sensitivity of electronic structure to small deviations from high symmetry. They indicate the need to distinguish between *octahedral* and *regular octahedral* as descriptions of the local symmetry of chemical bonding. The dichroism observed in ZnF_2 at the Zn K edge (Cox & Beaumont, 1980), where there are two Zn—F distances (2.01 and 2.04 Å) and F—Zn—F angles of 80, 90 and 100° (Baur, 1958), corresponds to an anisotropy of as much as 1.5 units. Comparable dichroism occurs in Fe_2O_3 (Dräger, Frahm, Materlik & Brümmer, 1988), where the distortion of the octahedron is even larger. In TiO_2

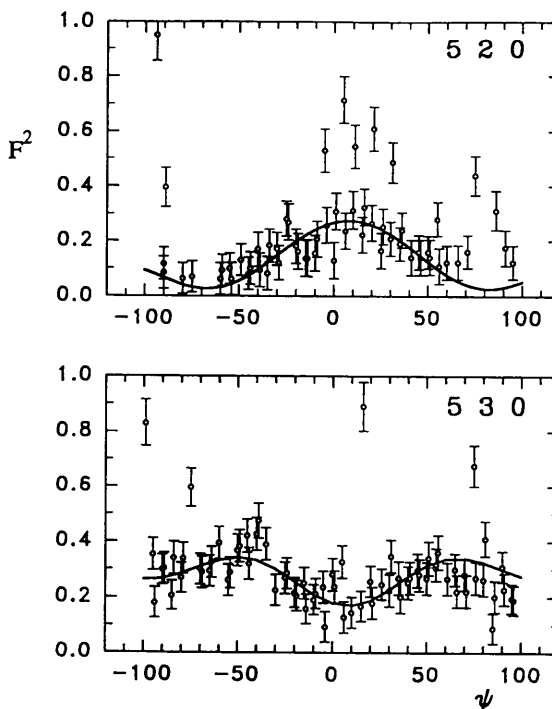


Fig. 3. Observed and calculated intensities of two forbidden reflections at 7120.4 eV.

and MnF_2 (isomorphous with ZnF_2), the anisotropy of f is sufficient for observation of a forbidden reflection (Kirfel, Petcov & Eichhorn, 1991) but no quantitative value was reported.

Evidence of quadrupole absorption was found at the first resonance (~ 7113 eV) in Fe_2O_3 and in FeCO_3 by Dräger, Frahm, Materlik & Brümmer (1988). Anisotropy of equivalent magnitude would not have been detected in these pyrite diffraction experiments. We are not able to estimate the absolute scale of the scattering measured by Finkelstein, Shen & Shastri (1992).

These results invite theoretical analysis in terms of the bonding orbitals in these several iron compounds.

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