Angle-independent Mössbauer effect in single-crystal pyrite

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The relative resonance intensity of the two Mössbauer transitions at ^{57}Fe sites in pyrite (FeS_2) is found experimentally to be unity (0.997 ± 0.004) and independent of the single-crystal orientation relative to the γ-ray direction. This result is consistent with a recent prediction of an angle-independent quadrupole interaction peculiar to the symmetry of pyrite and also demonstrates the recoilless fraction to be isotropic within experimental error.

The presence of an electric field gradient (EFG) at each Fe site in pyrite causes a two-line Mössbauer resonance associated with the $\Delta m = \pm\frac{3}{2}$ to $\pm\frac{1}{2}$ and $\Delta m = \pm\frac{1}{2}$ to $\pm\frac{1}{2}$ transitions in ^{57}Fe. In recent papers, Liu[1] evaluates the EFG tensor and mean-square-displacement (MSD) tensor for each of the four equivalent, but differently oriented, Fe sites in a unit cell. He arrives at a relation between the area ratio of the two Mössbauer resonance lines and the orientation of a single-crystal absorber of pyrite with respect to the angles of the incident γ ray. From this relation a vibrational anisotropy parameter can be determined experimentally as a function of the incident angles. Liu demonstrates from symmetry considerations that the quadrupole interaction is independent of these angles and therefore concludes that, for a single crystal of pyrite, the recoil-free fraction is isotropic (vibrational anisotropy parameter zero) if the area ratio is always unity independent of the crystal orientation.

Prior experimental work[2–4] as summarized in Table 5 of Ref. 4 reveals discrepancies in the obtained area ratios, several of which are different from unity. All of these experiments were carried out in the transmission mode using relatively thick absorbers of 50–200 μm. Because of thickness saturation effects,[5] a reduction of area-ratio sensitivity of about a factor of 3 or more can be expected in measurements using such thick absorbers.

To avoid this problem and difficulties in preparing thin sections of a pyrite single crystal, we observed the scattered 6.3-keV x rays produced by the internal-conversion process. The preference of the 6.3-keV x ray to the 14.4-keV γ rays lies in a higher count rate (internal-conversion coefficient of 8.2) and in the smaller effective thickness being sampled, about 20 μm, due to electronic absorption of the low-energy x ray.

The crystal used was a naturally occurring specimen which contained the following upper limits, in wt.%, of these elements according to x-ray fluorescence: P, 0.05; Si, 0.06; Ca, 0.03; Ti, 0.02; V, 0.02; Ni, 0.16; Cu, 0.09; Mo, 0.15; Ba, 0.02. The crystal was cut normal to a ⟨100⟩ axis and mounted such that the incident γ ray could be varied between a ⟨100⟩ and a ⟨110⟩ direction and defined by the angle θ shown in Fig. 1. Also shown in the figure is the data for an incident angle $\theta = 60°$.

The data reduction was done by least-squares fitting of Lorentzians to the experimental data. Due to the slight overlap of the two resonance lines (Fig. 1)

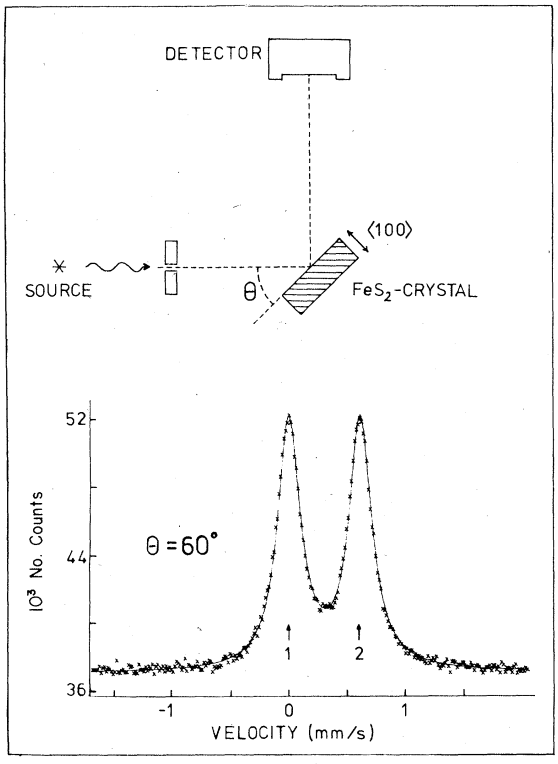

FIG. 1. Experimental set up and Mössbauer spectrum obtained with 6.3-keV internal-conversion x ray. The detector and crystal positions were adjustable such that data could be obtained for θ up to 90°.

TABLE I. Results from computer analysis of Mössbauer data. θ is the angle defined in Fig. 1. R is the ratio of resonance area (width × intensity) of line 1 to line 2 (Fig. 1) from fit of two independent Lorentzians. R' is the ratio of resonance intensity of line 1 to line 2 from fit of two lines with width constrained to be the same. Γ is the full width at half maximum (mm/s) obtained from the latter type of fit. The uncertainties shown represent one standard deviation of statistical uncertainty from the computer fits.

θ	R	R'	Γ
	Single crystal — scattering mode		
45 °⟨110⟩	0.997±0.014	0.994 ±0.007	0.241±0.001
60 °	1.009±0.016	1.001 ±0.008	0.238±0.001
70 °	0.965±0.021	0.995 ±0.011	0.236±0.001
80 °	1.036±0.037	0.998 ±0.018	0.237±0.002
90 °⟨100⟩	0.997±0.038	0.988 ±0.018	0.235±0.002
	0.997±0.009[a]	0.997 ±0.004[a]	
	Single crystal — transmission mode		
90 °⟨100⟩	0.999±0.010	1.000 ±0.004	0.389±0.002
	Powders — transmission mode		
Random		1.0002±0.0010[b]	0.235±0.001

[a]Weighted average. [b]Average of nine samples.

two types of fits were used: one which allowed independent widths and the other which forced the widths to be equal. For the latter type, the area ratio was thus reduced to an intensity ratio, resulting in smaller statistical uncertainties. Table I lists our results for various angles θ. We find all values of R and R' to be unity within one standard deviation with the exception of R for $\theta = 70°$ which is within 1.7 standard deviations. The weighted average of the intensity ratio R' over all samples is 0.997 ± 0.004.

In addition to the results from the scattering of the 6.3-keV x rays from the single crystal, Table I includes the result obtained from 14.4-keV γ-ray transmission through a single-crystal absorber of about 150-μm thickness and the result from transmission spectra of powder samples of 32-μm average particle size. Special care had to be taken in the preparation of the powder specimen due to the formation of $FeSO_4 \cdot H_2O$ (water soluble) in the grinding process. A small amount of this compound will cause the pyrite line 1 (Fig. 1) to appear more intense and could have been the cause of some of the discrepancies of earlier work.[2–4] The narrow linewidth obtained in the scattering mode compared to the transmission mode for the 150-μm specimen is indicative of the much smaller effective thickness sampled by the 6.3-keV x rays.

Thus, experimentally, the area ratio of the two resonance lines obtained from the Mössbauer spectra of a single crystal of pyrite is unity within error, and independent of the orientation of the crystal axes to the incident γ ray. This agrees with the theoretical work of Liu[1] and shows that the recoil-free fraction can be taken to be isotropic in pyrite. These conclusions are of current interest in the quantitative analysis of the pyrite content in coal and coal-derived products.[6] They permit one to disregard the orientation of pyrite crystals in a highly textured coal sample: for example, a determination of the amount of pyrite can be made solely from the observation of the intensity of one of the two lines in the Mössbauer spectrum.

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