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Electric field gradient and mean-square displacement of the iron sites in FeS_2 (pyrite)

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The electric-field-gradient tensor and the mean-square-displacement tensor (MSD) are considered for the four equivelent, but differently oriented, Fe sites in pyrite. Most of the parameters are obtained through symmetry considerations and a simple relation between the area ratio of the Mössbauer absorption peaks and the orientation of a single-crystal absorber is derived, which can be used to determine the MSD anisotropy parameter.

I. INTRODUCTION

The ^{57}Fe quadrupole splitting is given by

$$\Delta E_Q = \tfrac{1}{2} e^2 qQ (1 + \tfrac{1}{3}\eta^2)^{1/2} ,$$

where eQ is the nuclear quadrupole moment; eq is the largest principal value of the electric-field-gradient (EFG) tensor V_{ij}, i.e., $eq = V_{zz}$ when V_{ij} is diagonalized and with the convention $|V_{zz}| \geqslant |V_{yy}| \geqslant |V_{xx}|$; η is the asymmetry parameter $(V_{xx} - V_{yy})/V_{zz}$.

Mössbauer spectra of Fe-containing dichalcogenides of pyrite, and to a lesser extent the marcasite structures, have been studied with respect to their quadrupole splittings and magnetic properties. In this paper we consider in more detail the EFG of the pyrite structure taking iron pyrite, FeS_2, as an example and study the possibility of determining the mean-square-displacement tensor.

Iron sulfide with pyrite structure is a cubic crystal of cell constant $a_0 = 5.4179$ Å. The atoms are in the positions of T_h^6 ($Pa3$) symmetry,[1] i.e. the iron atoms occupy the positions at $(0,0,0)$, $(\frac{1}{2},\frac{1}{2},0)$, $(\frac{1}{2},0,\frac{1}{2})$, and $(0,\frac{1}{2},\frac{1}{2})$ and the S atoms are at $\pm(u,u,u)$, $\pm(u+\frac{1}{2},\frac{1}{2}-u,\bar{u})$, $\pm(\bar{u},u+\frac{1}{2},\frac{1}{2}-u)$, and $\pm(\frac{1}{2}-u,\bar{u},u+\frac{1}{2})$, with $u = 0.386$. The nearest neighbors of the iron atoms are the six sulfur atoms at distances of 2.26 Å, forming a distorted octahedron. The quadrupole splitting and its temperature dependence, the isomeric shift, as well as the magnetic properties of pyrite all indicate[2–5] that it is an Fe^{II} compound, with the Fe in a low-spin state $(3d^6)$. The area ratio, a_3/a_1, of the Mössbauer absorption peaks of a single crystal of FeS_2 pyrite has been studied[6] with γ rays, respectively, along the crystallographic axes a, b, and c, with a result that is consistent with an EFG tensor whose principal z axis is along a [111] direction and with an asymmetry parameter $\eta = 0$, in agreement with a simple point-charge-model calculation. Recently the absorption spectrum of a powder sample of pyrite in the presence of an external magnetic field has been studied[7,8] and it is concluded that e^2qQ is negative and that Fe does not possess a magnetic moment, while $\Delta E_Q = 0.65$ mm/sec. at 4.2 °K.

II. ELECTRIC FIELD GRADIENT

It is generally thought that the quadrupole splitting is a consequence of the distortion from octahedral symmetry caused by the two sulfur atoms along the [111] direction (i.e., the dumbbell). However, as shown in Ref. 6, the six nearest-neighboring sulfur atoms can also give an EFG tensor with a structure similar to what would be caused by the dumbbell. In fact, for the Fe at $(0,0,0)$, the nearest neighbors are the six S at $\pm(u-\frac{1}{2},\frac{1}{2}-u,\bar{u})$, $\pm(\bar{u},u-\frac{1}{2},\frac{1}{2}-u)$, and $\pm(\frac{1}{2}-u,\bar{u},u-\frac{1}{2})$. If each sulfur atom has an effective charge $-q_{\text{eff}}$, then the EFG with respect to the three axes a,b,c is

$$V_{ij} = (1-\gamma_\infty)\begin{pmatrix} 0 & A & A \\ A & 0 & A \\ A & A & 0 \end{pmatrix} , \qquad (1)$$

where γ_∞ is the Sternheimer antishielding factor, and with unit of length in Angström,

$$A = \frac{6 q_{\text{eff}} a_0^{-3} (u-\frac{1}{2})^2}{(3u^2 - 2u + \frac{1}{2})^{5/2}} = 0.0383 q_{\text{eff}} \qquad (2)$$

for the contribution from the nearest neighbors alone. The contribution from the dumbbell, i.e., S atoms at $\pm(u,u,u)$, would give

$$A = 2 q_{\text{eff}} a_0^{-3} (3u^2)^{-3/2} = -0.042 q_{\text{eff}} , \qquad (3)$$

whereas the contribution from all ions within a distance of 30 Å, with the effective S charge being $-q_{\text{eff}}$

and the Fe charge being $2q_{\text{eff}}$, is

$$A = 0.024 q_{\text{eff}} \, . \tag{4}$$

Only the dumbbell gives the correct sign of e^2qQ. If this is the only contribution, then the effective charge of the S atom should be $-1.5e$ for $\gamma_\infty \sim -11$,[9] and $Q \sim 0.21\text{b}$,[10] in order to give $\Delta E_Q \sim 0.65$ mm/sec. This would seem reasonable if the covalent FeS_2 bonds are the p_σ between Fe and the S atoms at the sites $\pm(u,u,u)$. One can then conclude that the electronic charge is at an average distance of

$$R_{\text{eff}} = (1.5)^{-1/3} R$$

from the Fe atom, with $R = 3.62$ Å being the distance between FeS and S.

Taking into account the symmetry of the crystal structure, or by a direct calculation based on a point-charge model, one can easily verify that for the $(0,0,0)$, $(\frac{1}{2},0,\frac{1}{2})$, $(\frac{1}{2},0,\frac{1}{2})$, and $(0,\frac{1}{2},\frac{1}{2})$ sites, the EFG tensors are, respectively, apart from the factor $(1-\gamma_\infty)$,

$$\begin{bmatrix} 0 & A & A \\ A & 0 & A \\ A & A & 0 \end{bmatrix}, \quad \begin{bmatrix} 0 & -A & -A \\ -A & 0 & A \\ -A & A & 0 \end{bmatrix},$$

$$\begin{bmatrix} 0 & A & -A \\ A & 0 & -A \\ -A & -A & 0 \end{bmatrix}, \text{ and } \begin{bmatrix} 0 & -A & A \\ -A & 0 & -A \\ A & -A & 0 \end{bmatrix}. \tag{5}$$

If one adopts the convention that

$$|V_{zz}| \geq |V_{yy}| \geq |V_{xx}| \, ,$$

then one obtains

$$\begin{aligned} V_{zz} &= 2A(1-\gamma_\infty) \, , \\ V_{xx} &= V_{yy} \\ &= -A(1-\gamma_\infty) \, , \end{aligned}$$

and

$$\begin{aligned} \eta &= (V_{xx} - V_{yy})/V_{zz} \\ &= 0 \, . \end{aligned} \tag{6}$$

The z axis is in the directions [111], [$-$111], [11$-$1], and [1$-$11], respectively, the x axis and the y axis are undetermined.

In Sec. III we shall analyze the consequences of these differences on the orientation of EFG principal axes and provide a procedure for obtaining MSD parameters.

III. MEAN-SQUARE DISPLACEMENT AND THE AREA RATIO

If $\langle x^2 \rangle$, $\langle y^2 \rangle$, and $\langle z^2 \rangle$ are the MSD along the principal axes, then for any direction $\hat{k}$ the MSD is given by[11]

$$\langle r^2 \rangle = \langle x^2 \rangle \sin^2\delta \cos^2\epsilon + \langle y^2 \rangle \sin^2\delta \sin^2\epsilon + \langle z^2 \rangle \cos^2\delta \, , \tag{7}$$

where δ and ϵ are the polar and azimuthal angles of $\hat{k}$. Hence if α, β, and γ are the three Euler's angles specifying the orientation of the MSD principal axes with respect to the crystallographic axes a, b, and c, then the MSD along these axes are

$$\begin{aligned} \langle r_a^2 \rangle &= \langle x^2 \rangle (\cos\alpha\cos\gamma - \sin\alpha\sin\gamma\cos\beta)^2 \\ &\quad + \langle y^2 \rangle (\sin\gamma\cos\alpha + \cos\gamma\sin\alpha\cos\beta)^2 \\ &\quad + \langle z^2 \rangle \sin^2\beta \sin^2\alpha \, , \\ \langle r_b^2 \rangle &= \langle x^2 \rangle (\cos\gamma\sin\alpha + \sin\gamma\cos\alpha\cos\beta)^2 \\ &\quad + \langle y^2 \rangle (\sin\alpha\sin\gamma - \cos\gamma\cos\alpha\cos\beta)^2 \\ &\quad + \langle z^2 \rangle \sin^2\beta \cos^2\alpha \, , \end{aligned}$$

and

$$\begin{aligned} \langle r_c^2 \rangle &= \langle x^2 \rangle \sin^2\gamma \sin^2\beta \\ &\quad + \langle y^2 \rangle \cos^2\gamma \sin^2\beta + \langle z^2 \rangle \cos^2\beta \, . \end{aligned} \tag{8}$$

Since for each Fe site the EFG z axis is a C_3-symmetry axis, we expect that

$$\langle r_a^2 \rangle = \langle r_b^2 \rangle = \langle r_c^2 \rangle \tag{9}$$

and one obvious solution to Eqs. (8) and (9) is that $\langle x^2 \rangle$, $\langle y^2 \rangle$, and $\langle z^2 \rangle$ are equal. However, there is a more general solution with two principal MSD being equal. Suppose $\langle x^2 \rangle = \langle y^2 \rangle \neq \langle z^2 \rangle$, one then obtains from Eqs. (7) and (8)

$$\alpha = \tfrac{1}{4}(2n+1)\pi$$

and

$$\beta = \cos^{-1}[1/(3)^{1/2}] \, , \tag{10}$$

while γ is undetermined. Therefore for each Fe site the MSD principal axes can be taken to coincide with the EFG axes.

For the thin-absorber limit, Zory[12] has shown that the area ratio of a quadrupole-split doublet $(I = \frac{3}{2} \rightarrow I = \frac{1}{2})$ associated with a single set of crystallographically equivalent sites is given by

$$\frac{a_3}{a_1} = \frac{\sum_i f_i(\theta_i, \phi_i) \{4[(3+\eta^2)/3]^{1/2} + (3\cos^2\theta_i - 1 + \eta\sin^2\theta_i \cos2\phi_i)\}}{\sum_i f_i(\theta_i \phi_i) \{4[(3+\eta^2)/3]^{1/2} - (3\cos^2\theta_i - 1 + \eta\sin^2\theta_i \cos2\phi_i)\}} \, , \tag{11}$$

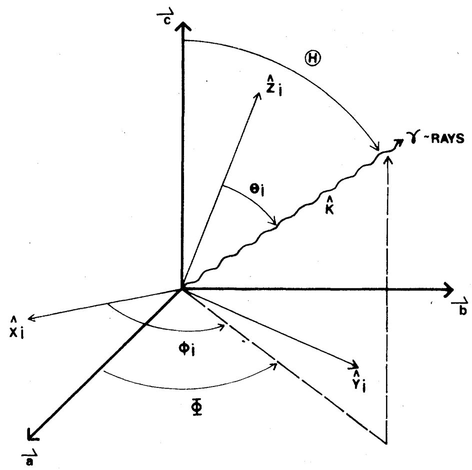

FIG. 1. Schematics of the absorption process of the 14.4-kev γ rays by ^{57}Fe, relative to the crystal axes (a,b,c) and to the EFG axes $(\hat{x}_i, \hat{y}_i, \hat{z}_i)$ of the i th site.

where the subscript i denotes the Fe site and θ_i, ϕ_i are the polar and azimuthal angles of the incident γ rays with respect to the EFG principal axes of site i and f_i is the recoil-free fraction given by[13–15]

$$f_i = e^{-k^2\langle r^2\rangle} ; \tag{12}$$

for $\langle x^2\rangle = \langle y^2\rangle$, this can be expressed as

$$f_i = \exp[-k^2(\langle x^2\rangle \sin^2\theta_i + \langle z^2\rangle \cos^2\theta_i)] , \tag{13}$$

where $\cos\theta_i$ is related to the experimental angles Θ and Φ through

$$\cos\theta_i = \sin\Theta\cos\Phi(\hat{z}_i\cdot\hat{a}) + \sin\Theta\sin\Phi(\hat{z}_i\cdot\hat{b}) + \cos\Theta(\hat{z}_i\cdot\hat{c}) \tag{14}$$

where $(\hat{z}_i\cdot\hat{a})$, $(\hat{z}_i\cdot\hat{c})$, and $(\hat{z}_i\cdot\hat{c})$ are the cosines of the angles between the EFG z axis and the crystallographic axes a,b,c, as shown in Fig. 1. The explicit expressions for $\cos^2\theta_i$ are given in Table I. With these expressions and relation (13) one obtains for a_3 and a_1

$$\begin{aligned} a_i \sim{} & \exp[-\tfrac{1}{3}k^2(2\langle x^2\rangle + \langle z^2\rangle)] \\ & \times([4 \pm \sin^2\Theta\sin2\Phi \pm \sin2\Theta(\cos\Phi+\sin\Phi)]\exp\{-\tfrac{1}{3}k^2\epsilon[\sin^2\Theta\sin2\Phi + \sin2\Theta(\cos\Phi+\sin\Phi)]\} \\ & + [4 \mp \sin^2\Theta\sin2\Phi \pm \sin2\Theta(-\cos\Phi+\sin\Phi)]\exp\{-\tfrac{1}{3}k^2\epsilon[-\sin^2\Theta\sin2\Phi + (-\cos\Phi+\sin\Phi)]\} \\ & + [4 \pm \sin^2\Theta\sin2\Phi \mp \sin2\Theta(\cos\Phi+\sin\Phi)]\exp\{-\tfrac{1}{3}k^2\epsilon[\sin^2\Theta\sin2\Phi - \sin2\Theta(\cos\Phi+\sin\Phi)]\} \\ & + [4 \mp \sin^2\Theta\sin2\Phi \pm \sin2\Theta(\cos\Phi-\sin\Phi)]\exp\{-\tfrac{1}{3}k^2\epsilon[-\sin^2\Theta\sin2\Phi + \sin2\Theta(\cos\Phi-\sin\Phi)]\}) , \end{aligned} \tag{15}$$

where $\epsilon = \langle z^2\rangle - \langle x^2\rangle$ is the anisotropy parameter and the upper and lower signs are for a_3 and a_1, respectively.

In principle one can determine the anisotropy parameter through Eqs. (11) and (15) by measuring the area ratios, as a function of Θ and Φ, of a thin absorber which is cut from a single FeS$_2$ crystal perpendicular to one of the crystallographic axes, e.g., the c axis. If the absorber is rotated around a fixed b axis, as depicted in Fig. 2, then $\Phi = 0$ and Eq. (11) reduces to

$$\frac{a_3}{a_1} = \frac{4\cosh\psi + \sin2\Theta\sinh\psi}{4\cosh\psi - \sin2\Theta\sinh\psi} , \tag{16}$$

where

$$\psi = \tfrac{1}{2}k^2\epsilon\sin2\Theta .$$

If the recoil-free fraction f is isotropic, i.e., $\psi = 0$ in Eq. (16), then $a_3/a_1 = 1$ for any angles Θ and Φ. So with a thin-single-crystal absorber, if the area ratio is always equal to unity independent of the orientation of the crystal, we may conclude that the recoil-free fraction is isotropic. However, when a powder sample is used, the fact that the area ratio is unity does not mean that f is isotropic. The reason for this is that when a_i is integrated over $d\Phi$, the angular-dependent parts contributed from different sites just cancel out. So a_3, a_1 is always equal to unity.

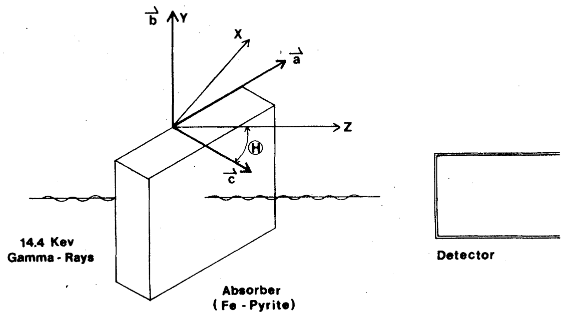

FIG. 2. Orientation of the absorber relative to the 14.4-kev γ rays in the determination of the MSD anisotropy parameter.

TABLE I. The expression for $\cos^2\theta_i$ (θ_i being the angle between the γ-ray direction and the EFG z axis) in terms of the experimental angles Θ and Φ.

Fe sites	Direction of EFG 3 axis	$\cos^2\theta_i$
000	(1,1,1)	$\frac{1}{3}[1+\sin^2\Theta\sin2\Phi+\sin2\Theta(\cos\Phi+\sin\Phi)]$
$\frac{1}{2}\frac{1}{2}0$	(−1,1,1)	$\frac{1}{3}[1-\sin^2\Theta\sin2\Phi+\sin2\Theta(-\cos\Phi+\sin\Phi)]$
$\frac{1}{2}0\frac{1}{2}$	(1,1,−1)	$\frac{1}{3}[1+\sin^2\Theta\sin2\Phi-\sin2\Theta(\cos\Phi+\sin\Phi)]$
$0\frac{1}{2}\frac{1}{2}$	(1,−1,1)	$\frac{1}{3}[1-\sin^2\Theta\sin2\Phi+\sin2\Theta(\cos\Phi-\sin\Phi)]$

IV. DISCUSSION

It is known that the bonds in FeS_2 are covalent, as pointed out in Ref. 6–8. Yet in Secs. I–III, the structures of the EFG tensors were calculated with the help of a point-charge model. It is worth noting, however, that the structure of the EFG tensors, and consequently that of the MSD tensors, depend only on the symmetry of the crystal, which is taken care of in the point-charge model. A detailed calculation using covalent bonding would only change the value of A in Eqs. (1) and (5), but this would not affect the conclusion reached in this paper about the directions of the EFG z axes of the Fe sites and the method for determining the anisotropy parameter.

Although the four Fe sites are equivalent, the fact that the crystal structure is of cubic symmetry requires that the EFG must either vanish at the Fe sites, which is contrary to the experimental fact that $\Delta E_Q \neq 0$, or that the EFG principal axes must be oriented in such a way that the averaged effects summed over the four sites must satisfy the given symmetry. It is this crystal symmetry that imposes a restriction on the EFG and also on the MSD, making it possible to determine both with a simple experimental procedure.

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