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NUCLEAR ELECTRIC FIELD GRADIENT OF THE IRON SITES IN FeS_2 (PYRITE)

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Résumé.- Les paramètres du tenseur gradient de champ électrique ont été calculés pour les quatre sites de fer équivalents - mais orientés différemment - de chaque cellule élémentaire de la pyrite. On trouve que les axes z pour les sites (0, 0, 0), (1/2, 1/2, 0), (1/2, 0, 1/2) et (0, 1/2, 1/2) sont respectivement dans les directions $\vec{a} + \vec{b} + \vec{c}$, $-\vec{a} + \vec{b} + \vec{c}$, $\vec{a} + \vec{b} - \vec{c}$ et $\vec{a} - \vec{b} + \vec{c}$; le paramètre d'assymétrie η est nul dans tous les cas. Si l'on suppose que la fraction d'effet sans recul est isotrope le rapport des aires a_3/a_1 pour le spectre Mössbauer d'un absorbeur monocristallin sera independant de son orientation et toujours égal à l'unité.

Abstract.- The electric field gradient tensor parameters were calculated for the four equivalent, but differently orientated sites of Fe in each unit cell of pyrite. It is found that the EFG z-axes for the sites at (0, 0, 0), (1/2, 1/2, 0), (1/2, 0, 1/2) and (0, 1/2, 1/2) are respectively in the directions $\vec{a} + \vec{b} + \vec{c}$, $-\vec{a} + \vec{b} + \vec{c}$, $\vec{a} + \vec{b} - \vec{c}$ and $\vec{a} - \vec{b} + \vec{c}$, the asymmetry parameter η being zero in all cases. If the recoil free fraction is isotropic, then the area ratio a_3/a_1, of the Mössbauer absorption spectra for a single crystal absorber will be independent of its orientation and always equals to unity.

Introduction.- Iron sulfide with pyrite structure is a cubic crystal of cell constant $a_o = 5.4179$ Å, Atoms are in the positions of T_h^6 (Pa 3) /1/, ie.Fe atoms occupy the positions at (0, 0, 0), (1/2, 1/2, 0), 1/2, 0, 1/2) and (0, 1/2, 1/2) and S atoms at $\pm$ (u, u, u), $\pm$ (u + 1/2, 1/2 - u, $\bar{u}$), $\pm$ ($\bar{u}$, u+1/2, 1/2 - u) and $\pm$ (1/2 - u, $\bar{u}$, u + 1/2), with u = 0.386. The nearest neighbors of Fe are the six S at distances Fe - S = 2.26 Å, forming a distorded octahedral. 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 a Fe^{II} compound , with the Fe in 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 result that is consistent with an EFG tensor of which the principale z-axis is along a [$\bar{1}$, 1, 1] direction and that $\eta = 0$, in agreement with a simple point charge model calculation. Recently absorption spectra of powder sample of pyrite in the presence of external magnetic field has been studied /7/ and it is concluded that e^2qQ is negative and that Fe posses no magnetic moment, while $\Delta E_Q = 0.65$ mm/s.

The 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 [$\bar{1}$, 1, 1] direction (ie the dumbbell) However, as shown in Ref. 6 that the six nearest neighboring S also can give an EFG tensor with a similar structure 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 - 1/2, 1/2 - u, $\bar{u}$), $\pm$ ($\bar{u}$, u - 1/2, 1/2 -u) and $\pm$ ($\bar{u}$, u - 1/2, 1/2 - u). If each sulfur atom has an effective charge $-q_{eff}$ then the EFG with respect to the three axes a, b, c is

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

where γ_∞ is the Sternheimer antishielding factor, and

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

$$= 0.0383\, q_{eff} / Å^3$$

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

$$A = 2q_{eff}\, a_o^{-3}\, (3u^2)^{-\frac{3}{2}} \qquad (3)$$

$$= -\, 0.042\, q_{eff} / Å^3$$

whereas contribution from all ions, with effective charge of S being $-q_{eff}$ and of Fe being $2q_{eff}$, is

$$A = 0.024\, q_{eff}/Å^3 \qquad (4)$$

Only the dumbbell gives correct sign of e^2qQ. If this is the only contribution, then the effective charge of the S atom should be -1.5e for $\gamma_\infty \sim -11$, in order to give $\Delta E_Q \sim 0.65$ mm/s. This would seem reasonable if the covalent bonding of FeS_2 are the μ_σ

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between Fe and the S atoms at the sites ± (u, u, u). One can then interpret that the averaged distance of the electronic charge is at a distance

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

from the Fe atom, with R = 3.62 Å being the distance Fe-S.

Taking into account of the symmetry of the crystal structure, or by direct calculation, one can easily verify that for the sites at (0, 0, 0) (1/2, 0, 1/2), (1/2, 0, 1/2) and (0, 1/2, 1/2) the EFG tensors are respectively, apart from the factor $(1 - \gamma_\infty)$,

$$\begin{bmatrix} 0 & A & A \\ A & 0 & A \\ A & A & 0 \end{bmatrix}, \begin{bmatrix} 0 & -A & -A \\ -A & 0 & A \\ -A & A & 0 \end{bmatrix}, \begin{bmatrix} 0 & A & -A \\ A & 0 & -A \\ -A & -A & 0 \end{bmatrix} \text{and} \begin{bmatrix} 0 & A & A \\ -A & 0 & -A \\ A & -A & 0 \end{bmatrix} \quad (5)$$

If one adopts the convention that $|V_{zz}| > |V_{yy}| > |V_{zz}|$, then one obtains,

$V_{zz} = 2 A (1 - \gamma_\infty)$

$V_{xx} = V_{yy}$

$= -A (1 - \gamma_\infty)$

and

$$\eta = (V_{xx} - V_{yy})/V_{zz} \quad (6)$$

$= 0$

The z-axis are in the directions [1, 1, 1], [-1. 1, 1], [1, 1, -1] and [1, -1, 1] respectively, the x-axis and the y-axis are indetermined.

In the next section we shall analyse the consequence of these differences in the orientation of EFG principle axis to the experimental area ratio.

The Area ratio.- Since the asymetry parameter is zero, then if the recoil free fraction is isotropic the area ratio of a quadripole splitting doublet is given by /8/

$$\frac{a_3}{a_1} = \frac{\sum_i \frac{5}{3} - \cos^2\theta_i}{\sum_i 1 + \cos^2\theta_i} \quad (7)$$

where θ_i is the angle between the incident 14.4 kev γ-rays and the EFG z-axis of the ith-site. It is related to the experimental angle Θ and Φ through

$$\cos\theta_i = \sin\Theta \cos\Phi\, (\hat{z}_i.\hat{a}) + \sin\Theta \cos\Phi\, (\hat{z}_i.\hat{b}) + \cos\Theta\, (\hat{z}_i.\hat{c}) \quad (8)$$

where $(\hat{z}_i.\hat{a})$, $(\hat{z}_i.\hat{b})$ and $(\hat{z}_i.\hat{c})$ are the cosines of the angles between the EFG z-axis and the crystallographic axes $\vec{a}$, $\vec{b}$, and $\vec{c}$, as shown in Figure 1. The explicit expressions for $\cos^2\theta_i$ are given in Table I.

When the incident γ-ray is along a crystallographic axis, Θ = 0 and Φ = 0, we have $\cos\theta_i = 1$ and hence $\frac{a_3}{a_1} = 1$.

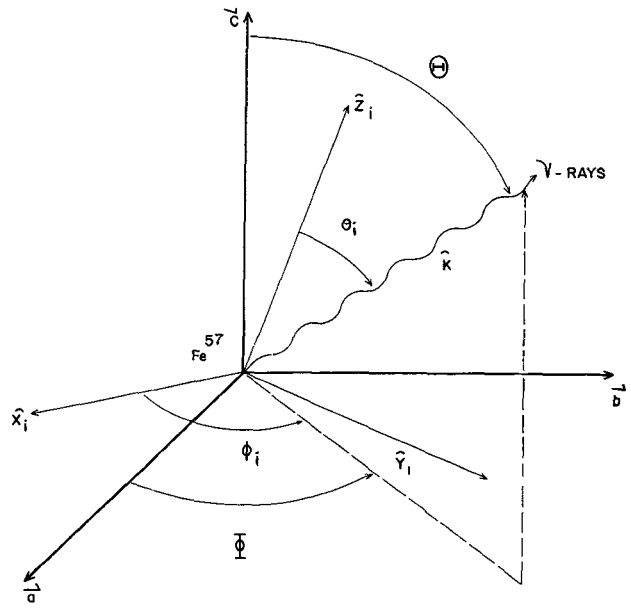

Fig. 1 : Schematics of the absorption process of the 14.4 kev γ-rays by ^{57}Fe, relative to the crystal axes (a, b, c) and to the EFG principle axes $(\hat{x}_i, \hat{y}_i, \hat{z}_i)$ of the ith site.

In reference (6) the EFG was calculated for the Fe-site at (0, 0, 0). The area ratio for γ-rays along $\vec{a}$, $\vec{b}$, or $\vec{c}$ axes were correctly predicted to be equal to unity while experimental observation was found to be approximately equal to 1, 0.9, 0.9. More careful experiments are being carried out /9/ and the preliminary results show that they are all consistent with unity. However, by taking into account of the different orientation of the EFG axes for the four equivalent Fe sites, we can also conclude that for arbitrary γ-ray direction, the area ratio must always be unity, as long as the recoil free fraction is isotropic. The reason for this is that, when summed over the four Fe-sites, the terms involving the azimuthal angle just cancel out each other and we have

$$\sum_{i=1}^{4} \cos^2\theta_i = \frac{4}{3}$$

which, when substituted into equation (7) gives

$a_3/a_1 = 1.$

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Table I

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

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

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