

## Mössbauer study of natural staurolite crystals

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**Abstract.** Mössbauer experiments have been carried out on natural crystals of staurolite at room temperature. The spectrum has been resolved into four doublets. From the intensity ratios of the quadrupole split doublets, the angles of the direction cosines of the electric field gradient for every site are determined when the gamma rays are parallel to *a*, *b* and *c*-axis of the crystal.

**Keywords.** Mössbauer study; staurolite; electric field gradient.

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### 1. Introduction

Mössbauer effect has been used for studying natural silicate minerals. Most of the studies are on polycrystalline samples and studies involving natural single crystals are few. This is because single crystals are associated with the presence of impurities in the mineral in the natural form. The present paper reports the Mössbauer effect study done on single crystals of staurolite.

Staurolite is a monoclinic (pseudo-orthorhombic nesosilicate) mineral in which  $\text{SiO}_4$  tetrahedra are isolated and are bound to each other only by ionic bonds through the interstitial cations. The mineral staurolite has the general formula,  $(\text{Fe}^{2+}, \text{Mg})_2(\text{Al}, \text{Fe}^{3+})_9\text{O}_6(\text{SiO}_4)(\text{O}, \text{OH})_2$  and is based on a unit cell containing 48 oxygen atoms in a cubic closed packing (Deer *et al* 1963). The crystal structure has  $\text{Fe}^{2+}$  and  $\text{OH}^-$  along planes parallel to (010) and alternate with layers of  $\text{Al}_2\text{O}$ .

The Mössbauer spectrum of staurolite was fitted to four doublets (Dejai 1978; Varma and Varma 1986). The peak assignment of Varma and Varma (1986) is based on the oxidation studies of staurolite by Varma and Varma (1987). Sharma *et al* (1987) however resolved the Mössbauer spectrum of staurolite in two doublets and one sextet. Although it has not been pointed out by them, staurolite very frequently has haematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) present in it as an impurity and can be separated using a strong magnet. The sextet in their spectrum is most probably due to the presence of haematite.

Single crystal studies on different crystallographic planes were carried out by Regnard (1976) who resolved the spectrum of staurolite into three doublets but the direction cosines of the electric field gradient were calculated for only one doublet. In this paper we report the values of the direction cosines of the electric field gradient of all the four doublets in the spectrum of staurolite.

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## 2. Theoretical considerations

The relative intensities of the quadrupole split peaks depend on the direction cosines of the wave vector of the  $\gamma$ -quanta with respect to the quantization axis. The intensity ratio  $I_2/I_1$  for the case of an axially symmetric field gradient tensor is given by

$$\frac{I_2}{I_1} = \frac{\left[ \int_0^\pi 3(1 + \cos^2 \theta) h(\theta) \sin \theta d\theta \right]}{\left[ \int_0^\pi (5 - 3 \cos^2 \theta) h(\theta) \sin \theta d\theta \right]}, \quad (1)$$

where  $\theta$  is the polar angle between the direction of the principal component of electric field gradient (EFG) and the  $\gamma$ -ray.  $h(\theta)$  is the function which describes the probability of finding an angle  $\theta$  between the directions of the z-axis and the  $\gamma$ -ray direction.

For an isotropic crystal the amplitudes of the atomic vibrations are a function of the direction. Karyagin (1963) and Goldanskii *et al* (1963a, b) have shown that the anisotropic crystals are accompanied by anisotropic Lamb Mössbauer factor  $f$  and for a polycrystalline sample even  $I_2/I_1$  does not turn out to be unity. For a single crystal however (1) takes the form

$$I_2/I_1 = 3(1 + \cos^2 \theta)/(5 - 3 \cos^2 \theta), \quad (2)$$

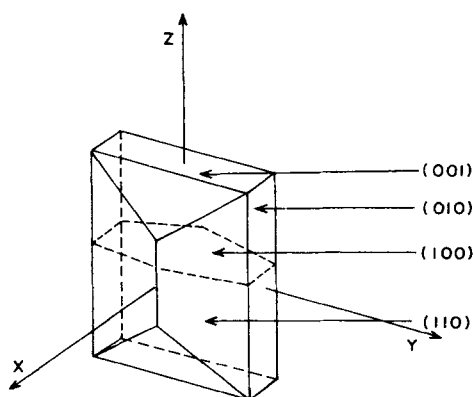
with values of  $I_2/I_1$  ranging from 3 for  $\theta=0^\circ$  to 0.6 for  $\theta=90^\circ$ . This ratio determined experimentally can be used to determine the value of  $\theta$ .

If three planes of a crystal are chosen which are perpendicular to the x-, y- and z-axis then the direction cosines of the EFG with respect to the crystal axis can be determined uniquely in most of the cases.

## 3. Experimental

The natural single crystal of staurolite chosen for the study was from the Udaipur region in Rajasthan, India. The crystal was 10 cm long with well-developed natural planes. The X-ray analysis of the mineral compared very well with that of staurolite. The few extra peaks present in the X-ray spectrum showed the presence of quartz in very small quantity. Nothing else was observed in the sample. The different crystallographic planes for the crystal were identified, sectioned and polished to uniform thickness of about 0.033 cm. This thickness is equivalent to 100 mg/cm<sup>2</sup> which, based on the average composition of staurolite, gives 6–7 mg of natural iron per square cm. The different planes chosen for the study were (001), (010), (100) and (110) and are shown in figure 1. The exact thicknesses of the different sections of the planes are given in table 1.

The spectra were recorded in the standard transmission geometry and the source used was a 40 mCi cobalt-57 in palladium matrix. Velocity was calibrated using a Laser Michelson's interferometer. The absorber was kept at room temperature. The spectra were recorded in the flyback mode. The data were computer-fitted using a nonlinear least-square fitting program for strongly overlapping peaks (Meerwall 1975).



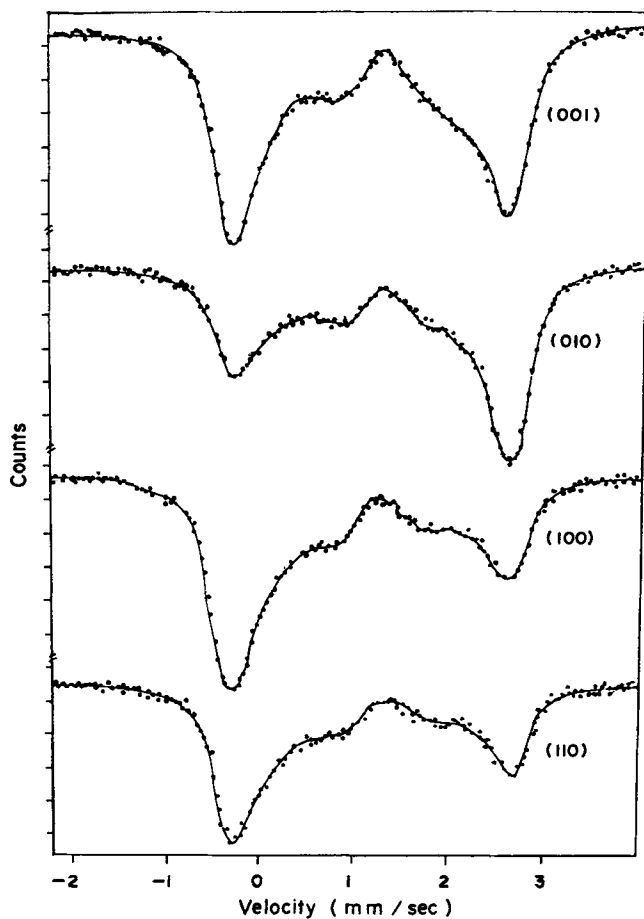
**Figure 1.** Crystal of staurolite mineral showing the different crystal planes.

**Table 1.** Different parameters of the different absorbers of staurolite crystal planes.

Plane	Average thickness (cm)	Surface area of the absorber (cm <sup>2</sup> )
(100)	0.035(5)	2.54(3)
(010)	0.040(5)	1.56(3)
(001)	0.029(5)	2.72(3)
(110)	0.029(5)	1.04(3)

**Table 2.** Room temperature isomer shifts (IS) (with respect to natural iron) in mm/sec and quadrupole splittings (QS) in mm/sec for different crystallographic planes of the staurolite crystal.

Plane	Doublet			
	AA'	BB'	CC'	DD'
(100)	IS 0.163(12)	1.022(75)	0.979(72)	1.108(82)
	QS 0.578(43)	2.183(161)	1.625(119)	0.678(51)
(010)	IS 0.197(15)	1.054(78)	1.040(77)	1.156(85)
	QS 0.626(46)	2.108(155)	1.632(77)	0.681(51)
(001)	IS 0.184(13)	1.027(76)	0.966(71)	1.142(84)
	QS 0.583(43)	2.156(159)	1.662(122)	0.694(51)
(110)	IS 0.231(17)	1.081(81)	1.040(77)	1.115(82)
	QS 0.660(48)	2.020(149)	1.476(109)	0.646(48)



**Figure 2.** Mössbauer spectra of different planes of staurolite crystal recorded at room temperature.

**Table 3.** Area ratios and the corresponding angles of the EFG for different sites for staurolite.

Plane	Doublets			
	AA'	BB'	CC'	DD'
(100)	0.755(21) $\theta_{Ax} = 67(2)^\circ$	1.535(16) $\theta_{Bx} = 38(1)^\circ$	2.000(61) $\theta_{Cx} = 28(1)^\circ$	0.837(21) $\theta_{Dx} = 62(1)^\circ$
(010)	2.449(4) $\theta_{Ay} = 21(1)^\circ$	1.732(13) $\theta_{By} = 90^\circ$	0.663(1) $\theta_{Cy} = 76(4)^\circ$	1.148(2) $\theta_{Dy} = 49(1)^\circ$
(001)	2.05(6) $\theta_{Az} = 27(1)^\circ$	0.71(3) $\theta_{Bz} = 71(2)^\circ$	0.86(6) $\theta_{Cz} = 60(3)^\circ$	0.99(3) $\theta_{Dz} = 55(1)^\circ$

#### 4. Results and discussion

The Mössbauer spectra for the four crystallographic planes at room temperature are shown in figure 2. Each spectrum was resolved into four doublets and the values of isomer shifts and quadrupole splittings of the different doublets for different planes are shown in table 2. The doublets AA' and DD' were assigned to Fe(3+) and BB' and CC' were assigned to Fe(2+) (Varma and Varma 1982). The intensity ratios of the two peaks of a doublet and the resulting angles for the different planes are shown in table 3. The values  $\theta_{Ax}$ ,  $\theta_{Ay}$  and  $\theta_{Az}$  are the angles that the EFG principal axis makes with the crystallographic axes for the A-site (which may be associated with iron in one site) and so on for the sites B, C, and D. The values of the angles for the site B as reported by Regnard (1976) compare very well with those reported here. In the structure of staurolite there is only one regular iron site which corresponds to the origin of the doublet BB'. The remaining peaks i.e. AA', CC' and DD' are associated with the iron substituted in two non-equivalent aluminium sites and/or electron sharing with two nearest ferric and ferrous sites.

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