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The electric field gradient and mean squared displacement tensor in 1M biotites investigated by Mössbauer spectroscopy

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Abstract. Detailed single-crystal studies of two biotites of the 1M polytype, containing respectively 6.7% and 11.5% by weight iron, are presented. Both the electric field gradient (EFG) and mean squared displacement (⟨MSD⟩) tensors are determined for Fe^{2+} in the *cis*- and *trans*-octahedral sites with considerable precision. Evidence of rather novel ordering of the iron in the sites is presented and the data fitted to two species (or two families of species) related by rotation of their EFG and ⟨MSC⟩ principal directions about the monoclinic axis.

1. Introduction

We have recently reported (Aldridge *et al* 1991) measurements of electric field gradient (EFG) in a thick crystal of biotite of the 1M polytype. Several features emerged. First, the EFG principal directions coincided apparently with the crystallographic axes and there seems no general expectation on symmetry grounds for this to be so. After appropriate thickness and polarization corrections we fitted our data to a single species in each of the *cis*- and *trans*-octahedral sites of the biotite structure. This fit, though reasonable, did not match the uncertainty in the measurements and we ascribed this to fitting errors arising from the necessity of fitting overlapping doublets in the single crystal. In particular we discussed in some detail the tendency of doublets to 'borrow' area from neighbouring doublets particularly at crystal orientations where the areas of individual wings of quadrupole doublets are far from equal. We chose our crystal carefully with a thickness for which we expected, from data presented by Grant *et al* (1969), to be able to make thickness and polarization corrections. However, we found that the procedures presented by these authors were not convergent in our crystal. Finally, as discussed by Aldridge *et al* (1991) the problem of adequately correcting for thickness and polarization in single crystals involving overlapping doublets has yet to be adequately addressed.

In this paper we attempt to resolve some of the above questions. We report EFG and mean squared displacement tensor, ⟨MSD⟩, measurements on two biotite single crystals of the 1M polytype (see the experimental and acknowledgments sections). The first, with a total iron content of 6.71% by weight, was chosen to have a 'thickness' of only 0.93 mg cm^{-2} total iron. We expected then that errors arising from overlapping peaks would not invalidate thickness and polarization corrections; we expect indeed that such corrections would be small anyway. Careful measurement of intensity ratios and total intensities produced data that were not explicable in terms of a single species in each of the *cis*- and *trans*-sites. We therefore studied a second biotite of the same polytype (total iron content, 11.54% by weight; thickness 4.04 mg cm^{-2} iron) and obtained, after thickness and polarization corrections, almost identical results. An explanation of these results in terms of rather novel ordering of the Fe^{2+} in the *cis*- and *trans*-sites of 1M biotite is presented. We present also, for the first time, accurate ⟨MSD⟩ tensor data for Fe^{2+} in these sites in 1M biotite. Application of the methods used to other, lower-symmetry, polytypes is discussed.

2. Experimental details

The two crystals chosen for study were from a collection of 1M biotites originating from the Smithsonian Institution, Washington DC, (see the acknowledgments). The first (USNM No 79000), hereafter labelled simply NY, was from Monroe, Orange County, NY, and the second (USNM No 96204), labelled USSR, originated from the Ilmen Mountains near Miask, USSR. The dimensions of each crystal chosen and cut for measurement was about 4 × 2 × 0.01 cm^3. NY contained 6.71% total iron by weight and USSR 11.54% total iron (atomic absorption analysis in both cases) by weight. The major element compositions as determined by x-ray fluorescence are listed in table 1.

Table 1. Chemical compositions of biotites studied[a].

Oxide	Percentage composition by weight	
	NY biotite	USSR biotite
SiO_2	41.31	39.53
Al_2O_3	12.83	12.14
TiO_2	1.16	1.30
Fe_2O_3[b]	0.74	2.94
MgO	20.83	16.89
FeO[b]	7.97	12.67
MnO	< 0.01	< 0.01
K_2O	9.68	9.35
Na_2O	1.06	1.20
CaO	< 0.01	< 0.01
LOI[c]	0.46	0.75

[a] Analytical data obtained by XRF.
[b] Fe_2O_3 and FeO from AA and Mössbauer results.
[c] LOI = loss on ignition at 1000 °C for 1 h.

All Mössbauer measurements were carried out on a PC-based ORTEC system together with ELSCINT drive electronics operated in the constant-acceleration mode. A ^{57}Co/Rh source of nominal strength 10 mCi was used as γ-source and iron foil used as velocity and chemical shift calibrant. Measurements were made in the coordinate system defined in figure 1. Some 12 orientations were measured with the γ-beam in the ac-plane of the crystal, measurements in this plane alone being in principle sufficient to the established principal axes of the EFG tensor (Aldridge *et al* 1991). Measurements in six other orientations ($\theta = 60°$ $\phi = 0°$, $\pm 30°$; $\theta = 45°$ $\phi = 0°$, $\pm 30°$) were also carried out. In principle both the EFG and ⟨MSD⟩ tensors are then well

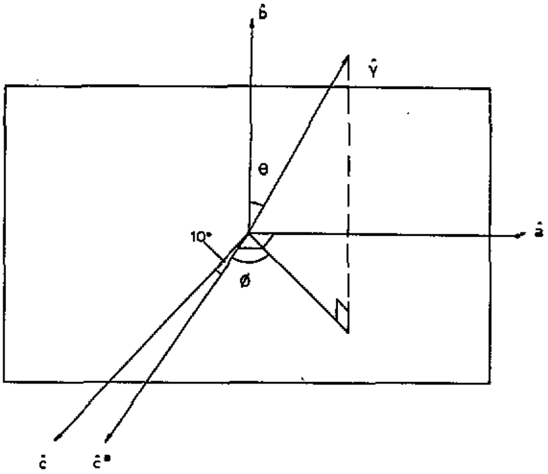

Figure 1. The coordinate system used in relation to the crystal axes a, b, and c. γ is an arbitrary unit vector along which the γ-beam is directed.

over-determined. It was arranged by appropriate collimation of the γ-beam and sample shielding that all γ-rays entering the detector had passed through the crystal. Count rates with and without 0.075 mm brass filter were determined for each crystal orientation and background corrections made as indicated by Grant *et al* (1969). At each crystal orientation some 3×10^6 background counts were accumulated.

3. Background theory

The appropriate theory and details of computer software developed to analyse single-crystal Mössbauer data from low-symmetry sites is presented elsewhere (Tennant 1992). In summary this program (MOSREF allows either simulation of intensity patterns for an isolated ^{57}Fe Mössbauer centre in a site of any (known) symmetry in a crystal of any (known) symmetry or, the refinement of Mössbauer parameters from an input set of measured single-crystal intensities. Both nuclear electric quadrupole and magnetic field interactions are included. As an extension to earlier such programs, provision is made for simulation of 'macroscopic' intensity tensors by including the ⟨MSD⟩ tensors and appropriate rotation matrices relating symmetry-related sites when more than one such site per unit cell exists, i.e. whenever the Laue class of the site is lower than the Laue class of the host crystal (see Gibb 1978). It is shown that simultaneous refinement of EFG and ⟨MSD⟩ tensors can in principle lead to the unique determination of the constituent 'macroscopic' EFG and ⟨MSD⟩ tensors. All calculations refer to the thin-crystal limit or data for which appropriate thickness and polarization corrections are possible. The program MOSREF is operated in arbitrary coordinates and utilises 'exact' numerical diagonalization of all matrices involved.

Biotite crystallography, appropriate to the Mössbauer experiment, for the 1M polytype has been discussed in detail by Aldridge *et al* (1991) and by Ballet and Amthauer (1986). Both the *cis*- and *trans*-sites must reflect the twofold symmetry of the crystal and the microscopic intensity tensors (see Zimmermann (1975) for definition) are in principle derivable with one principal axis lying along b and the other two lying in the ac-plane. The axis system is depicted in figure 1. The x, y,

z laboratory axes are taken to coincide with c^*, a and b, respectively, of the crystal system. We follow Aldridge *et al* (1991) in utilizing the cartesian tensor methods of Zimmermann (1975, 1983) in correcting and analysing our data; the detail is not repeated here. Thus from the background-corrected areas $I_{A,B}$ of the high- and low-velocity components of each quadrupole doublet we obtain the intensity ratios $I^{(r)} = I_A + I_B$ at each crystal orientation. First allowing for a factor $\cos(90 - \phi')$, where ϕ' is the angle between the γ-beam and the normal to the crystal plate, and then applying thickness and polarization corrections as described by Zimmermann (1983) and detailed by Aldridge *et al* (1991), we obtain the total intensities as $(p_A^{\cdot} + p_B^{\cdot})$ at each crystal orientation (the superscript $^{\cdot}$ implies correction to the thin-crystal limit). For the intensity tensor of an isolated species we have also the invariance condition

$$\tfrac{1}{3}\left[3I_{zz}^2 + \left(I_{xx} - I_{yy}\right)^2 + 4\left(I_{xy}^2 + I_{xz}^2 + I_{yz}^2\right)\right] = \tfrac{1}{6}. \qquad (1)$$

In principle program MOSREF allows us to obtain the best-fit EFG and ⟨MSD⟩ tensors by refining, respectively, the thickness- and polarization-corrected intensity ratio data and total intensity data each under the constraint of equation (1). The thickness and polarization corrections are carried out iteratively (in tandem with MOSREF) as detailed by Zimmermann (1983).

Aldridge *et al* (1991) outlined some difficulties involved in fitting Lorentzian areas to a suite of overlapping doublets of the ferrous and ferric sites of biotite. Hargraves *et al* (1990) in a recent paper have discussed at some length the difficulties in settling on a 'robust' technique of reliably fitting data from single crystals of the trioctahedral mica phlogopite. Here we follow Aldridge *et al* (1991) with the following modifications. As a first step, powder samples of each biotite were prepared by hand grinding the crystal under acetone in an agate mortar. A −200 mesh fraction of this powder was then further ground with glucose, again under acetone, to produce a mixture containing not more than 5 mg total iron per cm^2 of sample. A disc of this material was oriented at 55° to the γ-beam to eliminate any residual effects of preferred orientation and about 10^7 background counts accumulated. The resulting Mössbauer spectra were then fitted to Lorentzian areas (using program MOSFUN (Müller 1980)) to two pairs of ferrous and two pairs of ferric doublets using separate linewidths for ferrous and ferric. Attempts to fit a further doublet ascribed to tetrahedral ferric iron were not successful. The results of these powder fittings are listed in table 2. From the data of table 2 we obtained Lorentzian areas which we assumed proportional to the concentration of iron in each of the sites. It is noted that the Fe^{2+} *cis:trans* area ratio is 2:1 within experimental error. (The extent of overlap of doublets can be gauged from fittings depicted in figure 2 of Aldridge *et al* (1991).)

In the single-crystal fittings we applied the powder ratios as a constraint and assumed that the ratios of total peak areas of each of the Fe^{2+} *cis*- and *trans*-doublets and for each of the Fe^{3+} *cis*- and *trans*-doublets would remain constant over all single-crystal orientations. We then fitted both wings of the outer, most intense ferrous doublet but only one wing, namely the one at more positive velocity that is least overlapped in each case, for each of the other three quadrupole doublets. The data reported hereafter were obtained in this way. No reliable single-crystal area ratios could be obtained for the weak ferric doublets.

4. Results

In figures 2(*a*), (*b*) are plotted (full circles) the thickness- and polarization-corrected

Table 2. Mössbauer (powder) parameters for the biotites studied[a].

Sample[b]	Centre	Cis-site				Trans-site				Goodness of fit[c]		Background Counts
		IS	QS	LW	Area %	IS	QS	LW	Area %	χ^2	Misfit	
NY(1)	Fe^{2+}	1.127(2)	2.566(5)	0.331(4)	60.6(1.5)	1.119(5)	2.178(12)	0.331(4)	31.7(1.3)	753	0.00065	9.05 M
	Fe^{3+}	0.57(7)	1.17(10)	0.31(3)	2.3(5)	0.54(2)	0.57(3)	0.31(3)	5.4(6)			
NY(2)	Fe^{2+}	1.123(2)	2.567(5)	0.330(4)	60.4(1.5)	1.115(6)	2.180(10)	0.330(4)	31.8(1.3)	753	0.00065	9.05 M
	Fe^{3+}	0.56(10)	1.17(15)	0.330(4)	2.1(5)	0.54(2)	0.58(3)	0.330(4)	5.7(5)			
USSR(1)	Fe^{2+}	1.104(1)	2.575(5)	0.311(4)	54.8(1.2)	1.084(4)	2.221(11)	0.311(4)	27.3(1.0)	779	0.00065	3.01 M
	Fe^{3+}	0.52(2)	0.95(4)	0.36(3)	8.7(1.0)	0.47(2)	0.57(3)	0.36(3)	9.1(1.1)			
USSR(2)	Fe^{2+}	1.105(1)	2.572(5)	0.314(4)	56.0(1.2)	1.083(4)	2.208(13)	0.314(4)	26.8(1.1)	789	0.00066	3.01 M
	Fe^{3+}	0.52(2)	0.96(3)	0.314(4)	8.6(7)	0.47(1)	0.54(2)	0.314(4)	8.6(7)			

[a] IS = isomer shift; QS = quadruple splitting; LW = linewidth (FWHM), all expressed in mm s^{-1} with respect to natural iron. Figures in parentheses denote 95% confidence uncertainties in the last significant figures.

[b] (1) Fe^{2+} linewidths constrained to be equal but different from Fe^{3+} linewidths; (2) all linewidths constrained to be equal.

[c] For definitions of χ^2 and misfit, see Dyar (1984).

area ratios $I_A/(I_A+I_B)$ for each of the *cis*- and *trans*-sites in USSR biotite. The best-fit theoretical curve assuming one isolated Mössbauer centre is also plotted (dashed line). A least-squares analysis of the experimental data based on a curve of the form $I = A + B\cos 2\phi + C\sin 2\phi$ indicates measurement errors of the order of 0.002 intensity units. The fittings errors are, however, an order of magnitude greater than this. We confirmed by x-ray crystallography that the polytype (1M, space group $C2/m$ monoclinic) and the crystal alignment were correct. We are therefore led to the conclusion that, either the fitting procedure is faulty or that the crystals are disordered in some way, i.e. that there is, despite the expectations based on $C2/m$ space group symmetry, a 'family' of EFGs and that we observe only a macroscopic intensity tensor. Such disordering could be envisaged to occur as a result of different next-nearest-neighbour cations in adjacent *cis*- and *trans*-sites, as has been discussed by Manceau *et al* (1990), due to F^- ions replacing OH^- ions in the biotite structure. (There is also the possibility of 'texture' in the crystals which is addressed below.

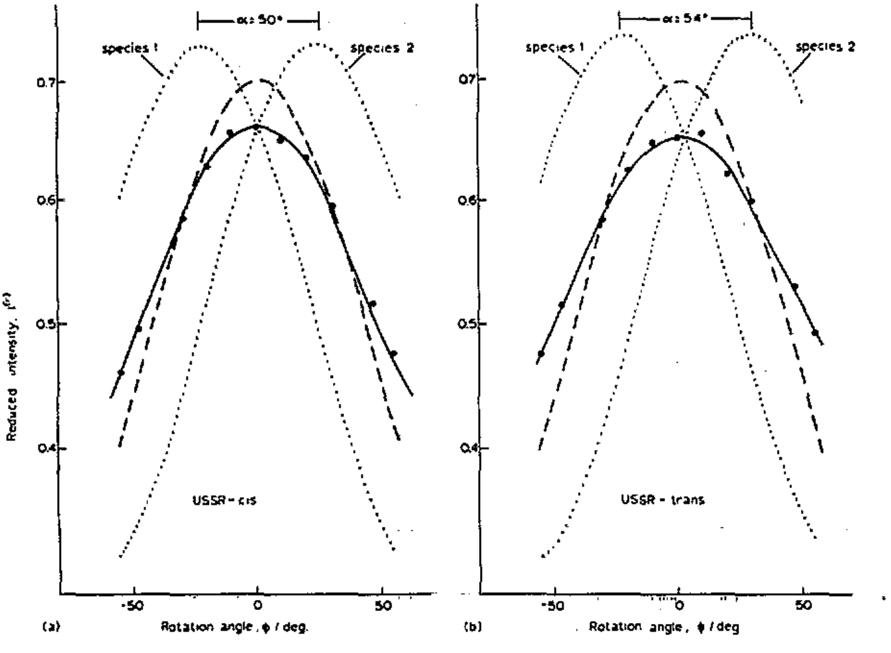

Figure 2. Angular dependence of reduced intensity, $I^{(r)}$, in the ac-plane of the USSR biotite crystal: (*a*) Fe^{2+}/*cis*, (*b*) Fe^{2+}/*trans*. Key: ●, experimental points; - - - -; best fit for single species; · · · · · ·, calculated curves for species 1 and 2; ——, best-fit curve for two species (see the text for details).

Disorders of these types must however obey the laws of crystal symmetry. The family of EFGs (and indeed ⟨MSD⟩s) must all have in common the two-fold axis of the monoclinic structure. The parameter refinement program, MOSREF, allows refinement over the symmetry-related sites in the unit cell by reading in the appropriate Euler rotation matrices. A small modification of this procedure is to allow rotation of different EFGs about a common axis by reading in an Euler rotation matrix with variable rotation angle α. However, to resolve the ambiguity involved in two or more EFGs that contribute to the same quadrupole doublet we must be able to measure with reasonable precision anisotropy in the sample recoil-free fraction (Goldanskii–Karyagin effect GKE)—typically for iron compounds a very small effect. In the thin-crystal limit the total areas are related to the recoil-free-fraction, f', by (see Grant *et al* 1969)

$$(p_{\mathrm{A}}^{\cdot} + p_{\mathrm{B}}^{\cdot}) \cos \phi' = n_{\mathrm{f}} \sigma_0 f' \tag{2}$$

where σ_0 is the resonant cross section per Mössbauer nucleus ($= 2.56 \times 10^{-18}$ cm^2 for ^{57}Fe (Gütlich *et al* 1978)) and n_{f} the number of Mössbauer nuclei.

In figures 3(*a*), (*b*) are plotted for each of the *cis*- and *trans*-sites the recoilless fractions, f', for the USSR and NY biotites evaluated, following thickness and polarization corrections from equation (2). There is a small but definite curvature (anisotropy) in the plot of recoilless fraction versus angle in the ac-plane of the crystals even although they have been derived from individual areas $p_{\mathrm{A}}^{\cdot}, p_{\mathrm{B}}^{\cdot}$ whose plots versus angle ϕ exhibit opposite curvature in each case.

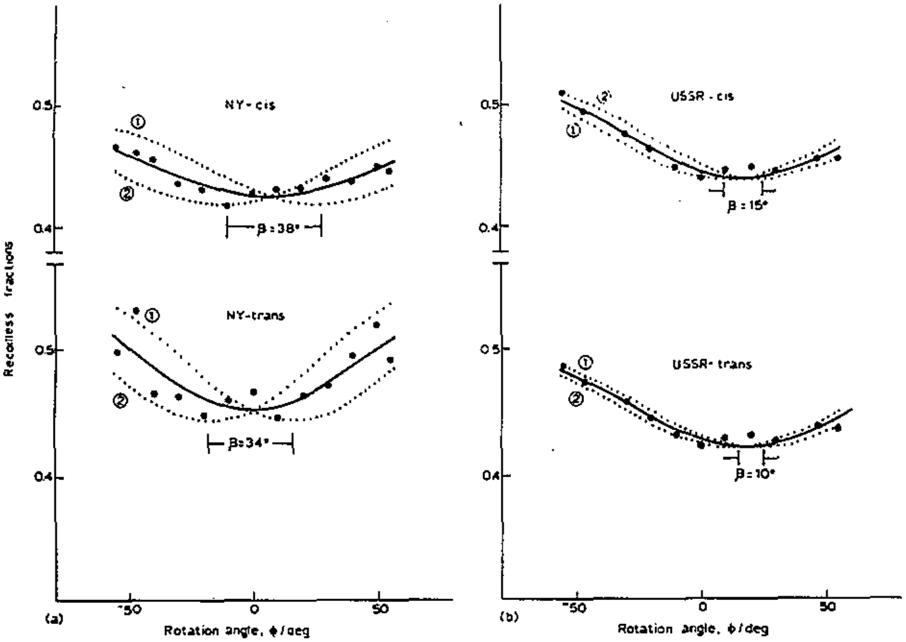

Figure 3. Angular dependence of recoilless fractions for Fe^{2+} in the *cis*- and *trans*-sites of the two biotites (key as for figure 2; see the text for details).

To check the above conjectures for two sets, the program MOSREF was used to fit simultaneously two EFGs and two ⟨MSD⟩s where the EFGs are related by rotation angle α in the ac-plane and the ⟨MSD⟩s are related by angle β in the ac-plane; initially we took $\alpha = \beta$. With this procedure there was an immediate drop of fitting errors by an order of magnitude and an excellent fit to both intensity ratio and total intensity data. These results are shown as the solid lines in figures 2(*a*), (*b*) and 3(*a*), (*b*). The dotted lines in each case are the plots for the contributing species which we shall henceforth refer to as species 1 and species 2. The rotation angles α (USSR only) and β (USSR and NY biotites) are also shown in the figures.

The final fitted values of the angles α and β together with their error estimates are (in degrees) as follows. USSR-*cis*: $\alpha = 50.1 \pm 0.8$, $\beta = 15 \pm 18$; USSR-*trans*: $\alpha = 53.6 \pm 0.7$, $\beta = -10 \pm 17$; NY-*cis*: $\alpha = 51.5 \pm 1.1$, $\beta = -38 \pm 24$; NY-*trans*: $\alpha = 52.5 \pm 1.2$, $\beta = -34 \pm 17$. The parameters determined for each of the Fe^{2+} sites are summarized in table 3 together with their error estimates. The principal values and directions of the EFG tensors are well determined. The principal values of the ⟨MSD⟩ tensors, and corresponding recoilless fractions, are also well determined but the principal directions are not particularly well determined due to low precision in the determining angle β. Unfortunately this impression also affects the value of the asymmetry parameter, η, which is not as well determined as we would have hoped.

5. Discussion

From figures 2 and 3 and table 3 it is apparent that an excellent fit is obtained for the Mössbauer single-crystal for each of the biotites studied. That this fit is obtained for two species may however be fortuitous and we cannot rule out the possibility of a family of EFGs and ⟨MSD⟩s each having in common the twofold rotation axis of the monoclinic crystal. Nevertheless it is worthwhile to examine the solutions obtained further and, in particular, to consider the alignments of the principal directions of the EFG and ⟨MSD⟩ tensors in relation to the local site symmetry. In figures 4(*a*), (*b*) are shown ORTEP plots (Johnson 1971) of the EFG principal directions for the USSR biotite in two adjacent *cis*- and *trans*-sites where we have followed earlier publications (Aldridge *et al* 1987, 1991) and depicted the bonding octahedra in each case. In figure 4(*a*) the unit cell has been rotated, from an initial c-axis projection, 15° about *b* in a clockwise sense, and in 4(*b*) −30° clockwise about *b* followed by a 5° clockwise rotation about *a* to depict the tensor axes better in each case.

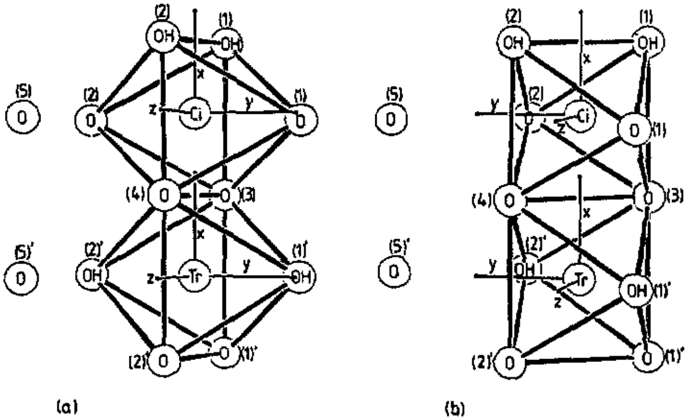

Figure 4. Traceless intensity (EFG) tensor principal directions for the USSR biotite in relation to the *cis*- and *trans*-bonding octahedra: (*a*) species 1; (*b*) species 2 (see the text for details).

Consider first species 1 (figure 4(*a*)) in the USSR biotite. As required by crystal symmetry, one principal direction ($I_{\hat{x}\hat{x}}$–$V_{\hat{x}\hat{x}}$), lies along the *b*-axis. $I_{\hat{y}\hat{y}}$ lies almost

Table 3. Intensity tensor and ⟨MSD⟩ tensor principal values (I_{pp} and $\langle pp\rangle$, $p = x, y, z$) and principal directions[a].

Centre	**EFG Tensors**					**<MSD> Tensors**				
		Principal Values	**Principal Directions**[b]			**Principal Values**	**Recoilless Fractions**	**Principal Directions**[b]		
	pp	**Ipp**	**θ**	ϕ_1	ϕ_1'	$\langle pp\rangle/10^{-18}\mathrm{cm}^2$	**f′**	**θ**	ϕ_2	ϕ_2'
USSR-cis	zz	-0.234(3)	90	-22.8(2)	27.3(2)	1.269(11)	0.508(5)	90	101(18)	116(18)
	xx	0.042(3)	0	-	-	1.548(6)	0.438(2)	90	11(18)	26(18)
	yy	0.182(10)	90	67.2(4)	-62.7(4)	1.619(50)	0.422(13)	0	-	-
	η =	0.642(43)								
USSR-trans	zz	-0.239(3)	90	-24.7(2)	28.9(2)	1.351(26)	0.487(9)	90	113(17)	103(17)
	xx	0.055(3)	0	-	-	1.616(25)	0.423(7)	90	23(17)	13(17)
	yy	0.184(10)	90	65.3(4)	-61.1(4)	1.680(46)	0.408(11)	0	-	-
	η =	0.538(40)								
NY-cis	zz	-0.242(4)	90	-24.1(3)	27.5(3)	1.216(15)	0.523(6)	0	-	-
	xx	0.066(4)	0	-	-	1.371(27)	0.481(9)	90	116(24)	258(24)
	yy	0.176(12)	90	65.9(6)	-62.5(6)	1.630(80)	0.419(21)	90	26(24)	-12(24)
	η =	0.455(60)								
NY-trans	zz	-0.246(4)	90	-24.5(2)	28.0(3)	1.128(21)	0.548(10)	90	106(17)	252(17)
	xx	0.086(4)	0	-	-	1.413(38)	0.471(13)	0	-	-
	yy	0.160(12)	90	65.5(6)	-62.0(6)	1.521(13)	0.445(4)	90	16(17)	-18(17)
	η =	0.302(60)								

[a] Error estimates in parentheses.

[b] Angles in degrees; $\phi_1' - \phi_1 = \alpha$ and $\phi_2' - \phi_2 = \beta$ (see the text).

along the Fe–O(1) vector in the *cis*-site and close to Fe–OH(1) vector for the *trans*-site (the angles made with these directions are, respectively, 1.4° and 5.6°). $I_{\hat{z}\hat{z}}$ for the *cis*-site lies 7.6° away from the line joining Fe^{2+} to the bisector of O(4),OH(2) while in the *trans*-site $I_{\hat{z}\hat{z}}$ lies 4.3° away from the line joining Fe^{2+} to the bisector of O(2)′, O(4).

The principal EFG directions for the second species are similarly sensibly directed with respect to the surrounding atoms. Thus, from figure 4(*b*), $I_{\hat{x}\hat{x}}$ again lies along *b* in both *cis*- and *trans*-sites, $I_{\hat{x}\hat{x}}$ lies 1.1° away from the line joining Fe^{2+} to the centroid of atoms O(2),O(4),OH(2) in the *cis*-site and 5.1° away from the line joining Fe^{2+} to the centroid of atoms O(2)′,O(4),OH(2)′ in the *trans*-site. $I_{\hat{x}\hat{x}}$ lies 17.9° away from the line joining Fe^{2+} to the centroid of atoms O(1),O(4),OH(2) in the *cis*-site and 17.6° away from the line joining Fe^{2+} to the centroid of atoms O(2)′,O(4),OH(1)′ in the *trans*-site. The $I_{\hat{x}\hat{x}}$ principal directions also lie very close to the directions Fe–O(5) and Fe–O(5)′ for the *cis*- and *trans*-sites respectively where O(5) and O(5)′ are next-nearest-neighbour oxygens lying 3.68 Å away from the iron centres. It is clear from the data of table 3 that the results for the NY biotite are closely similar.

For the alignment of the ⟨MSD⟩ tensors rather different results are expected. Grant *et al* (1969) have proposed that the principal directions of the ⟨MSD⟩ tensor would be governed by long-wavelength vibrations in the crystal which may be expected to reflect the basic symmetry of the lattice rather than the local symmetry of the Mössbauer centre. In compliance with this they showed that the principal directions of the ⟨MSD⟩ tensor in sodium nitroprusside lie almost along the crystallographic axes. It is of some interest in the present instance therefore that the ⟨MSD⟩ tensors for species 1 and 2 in the *cis*- and *trans*-sites in both biotite crystals show a tendency to lie along the crystal axes although, as shown by the parenthesized errors of table 3, there is considerable uncertainty in the principal directions. Again as demanded by symmetry considerations one principal direction lies along *b* and the others lie, within error, close to *a* and *c*. There is no requirement for the remaining two principal directions in the *ac*-plane to coincide with the EFG principal directions and indeed they do not.

The above gives a coherent description of the biotite Mössbauer intensities in two biotite single crystals of the 1M polytype. There are, however, other possibilities which must be considered. These are: (i) mosaics of crystalline plates aligned on average perpendicular to $c*$, the normal to the basal plane of the mica—i.e., the crystal is not strictly a single crystal; (ii) disordered stacking sequences—for example, the present results could just as readily be accounted for by two preferred orientations of plates related to one another by a 180° rotation about the normal to the crystal; or (iii) families of EFGs and ⟨MSD⟩s, rather than just two of each tensor, resulting as discussed earlier from differences in next-nearest neighbours.

Possibilities (i) and (ii) can be examined by x-ray crystallography: each would be expected to result in satellites or multi-reflected diffractions on or adjacent to the *c*-axis. We examined Weissenberg x-ray photographs of a portion of the NY biotite and showed that the appropriate reflections, apart from a minor 'ghost' attributed to the effect the crystal cleaving during preparations, were normal and resolved. We conclude that the crystal is indeed single and texture and/or packing of the type described in (i) and (ii) above is effectively absent.

There remains therefore only (iii) to consider and this cannot easily be refuted. However, the fact that closely similar two-species fits of the data for two different biotites of differing origins are obtained seems highly significant. Whether this indicates two families of tensors spread about the directions given, and to what extent this spread occurs, cannot at this stage be assessed.

It is also interesting to speculate on whether this behaviour is widespread amongst biotites of the 1M polytype. We are currently carrying out further work on the biotite crystal reported by Aldridge *et al* (1991) (iron content 18.9% by weight) using cleaved plates. Preliminary results indicate closely similar results to those reported in this paper. We are also attempting to determine, from a study of plates of varying thickness from this crystal, how to assess thickness and polarization corrections in crystals of moderate thickness where overlapping of doublets occurs. This is a possible source of error in this present work whose ramifications cannot at this stage be assessed. However, as noted earlier, we chose very thin crystals and expected that the errors would be quite small. We found in fact that the intensity ratios of corrected and uncorrected data never varied by more than 0.4% for NY and never more than 1.5% for USSR. Neglect of thickness and polarization corrections would have resulted in 2% and 8% underestimates of recoilless fractions in NY and USSR respectively. The similarity of the results obtained from crystals whose iron contents differ by a factor of about two and whose effective thicknesses vary by a factor of about four would tend to confirm the validity of the corrections.

The values of the asymmetry parameter, η, obtained for the two biotite crystals in this study require some comment (see table 3). Certainly the expectations of a low-symmetry site are borne out: η differs considerably from zero. Also η is numerically larger for the *cis*-site in each biotite. This is as expected having regard for the known more symmetric nature of the *trans*-octahedron which also shows up in quadrupole splittings: the *cis*-site has a larger splitting than does the *trans*-site (see table 2). Our earlier study of a biotite, which did not take into account ordering of the type considered here, obtained rather smaller values for η and the relative magnitudes of the *cis*- and *trans*-values were reserved. We believe our present results to be more reliable and hope in further work to obtain the asymmetry parameter more precisely by a more precise measurement of the $\langle$MSD$\rangle$ tensor.

The rather large difference in asymmetry parameter, in excess of the combined errors, between the two biotites studied is unexpected. It would seem that increasing the amount of iron in the octahedral layer of biotite results in considerably increased distortion of the iron-containing *cis*- and *trans*-sites. This is certainly possible, but we would expect this distortion to be mirrored also in rather different quadrupole splittings in the two crystals. Table 2 shows only a small increase in quadrupole splitting for the USSR biotite over the NY sample; we are unable to comment on the significance of this.

Recoil is of course a fundamental physical property in Mössbauer spectroscopy and it is of considerable interest in the present instance to compare mean squared displacements of the Fe^{2+} centres as determined by the Mössbauer experiment with those determined from thermal factors in x-ray crystallography. Equivalent temperature factors, B, for *cis*- and *trans*-sites in biotite are (Ohta *et al* 1982) respectively 0.71 Å^2 and 0.85 Å^2 from which we obtain the mean squared displacements, $\langle r^2\rangle$, 0.899×10^{-18} cm^2 and 1.076×10^{-18} cm^2 respectively. From table 3 the 'isotropic' recoil-free fractions in both the *cis*- and *trans*-sites average 0.465. Using the relation $f' = \exp(-k^2\langle r^2\rangle)$ and taking (Grant *et al* 1969) $k^2 = 5.33 \times 10^{17}$ cm^2 we obtain from our Mössbauer measurements $\langle r^2\rangle = 1.447 \times 10^{-18}$ cm^2. That is, the mean squared displacements from Mössbauer in the *cis*- and *trans*-sites are larger by factors of about 1.6 and 1.4 respectively than those obtained from equivalent x-ray-determined temperature factors (both sets of measurements refer to 25 °C). The values are rather smaller than that found by Grant *et al* (1969) in sodium nitroprusside. In the biotite case it needs to be recognized that the thermal factors are averaged over the atoms (Fe,Mg,Ti etc) of the *cis*- and *trans*-sites rather than just for iron. It would be useful to be able to comment on anisotropy in the recoilless fractions in specific directions in the crystal but at this stage the errors are such as to make this too uncertain.

6. Conclusions

We have, by simultaneous measurement and determination of EFG and ⟨MSD⟩ tensors for Fe^{2+} in the *cis*- and *trans*-sites in the octahedral layer of two 1M biotites, detected what we believe to be evidence of rather novel ordering of Mössbauer species in the two sites. The EFG and ⟨MSD⟩ tensors for species 1 and 2 have both been determined and their principal directions related to local and/or lattice symmetry.

There is a need now to examine further the low-temperature magnetic splitting in biotite crystals in applied magnetic fields. Such measurements have thus far been restricted to crystals of unspecified polytype and ordering of the type postulated here for 1M biotites is likely to have a profound effect on the magnetism.

The fact that EFG and ⟨MSD⟩ tensors can be determined with considerable precision make it useful to pursue cluster calculations by, for example, $X\alpha$-scattered wave or molecular orbital methods, to test experimental results with calculated EFGs.

Finally the difficulty of making thickness and polarization corrections in crystals of finite thickness with overlapping quadrupole doublets has yet to be adequately addressed. Such corrections are necessary to extend the current measurements to high-iron-content biotites. Some of these calculations and experiments are in progress and will be reported subsequently.

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