

## Lattice sum calculations and a Mössbauer study on electric field gradient in phlogopite

ANJALI KRISHNAMURTHY, BIPIN K SRIVASTAVA and  
S LOKANATHAN

Department of Physics, University of Rajasthan, Jaipur 302 004, India

MS received 20 September 1980; revised 8 December 1980

**Abstract.** Lattice sum contributions have been calculated at the two octahedral sites in a phlogopite mica assuming a systematic distribution of octahedral cationic charges. This, unlike the case of a random distribution of charges, is able to reproduce broad features of quadrupole doublet spectra in Mössbauer experiments suggesting that the doublet assignments in terms of the two structural sites,  $M_1$  (trans) and  $M_2$  (cis), are quite valid. Angle dependence of Mössbauer spectra has also been studied for a ferric-rich phlogopite mica sheet to determine the orientation of the EFG principal axis component and the sign of the quadrupole coupling constant. Quadrupole splitting values and the positive sign of coupling constants match the theoretical predictions quite well but the model fails to predict the observed EFG orientation.

**Keywords.** Electric field gradient; mica; Mössbauer spectra; lattice sum calculations; point charge model; phlogopite.

### 1. Introduction

Mössbauer spectra of mica using iron ( $^{57}\text{Fe}$ ) have been studied extensively and despite their complex structure have certain broad features. For instance iron mostly occupies octahedral sites and occurs as  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  giving rise to pairs of quadrupole doublets. Beyond this stage, a wide range of hypotheses has been proposed and the experimental data have not clarified the basic question of cationic ordering. To this is directly related the question of Mössbauer doublet assignments. While several experimental studies have favoured assignments in terms of the structural sites, some theoretical calculations present an opposite picture. One version studied by Goodman (1976 b) is that there is a random distribution of defect charges around both inequivalent sites so that the Mössbauer spectra ought to result from considerably fluctuating environment. The opposite extreme studied in this paper is that there is a systematic distribution of octahedral cationic charges. To interpret the Mössbauer spectra in micas, an understanding of the extent to which these admittedly over-simplified hypotheses agree with the experimental parameters is important.

Micas are layered sheet silicates and phlogopite mica, the subject of this paper, crystallizes in the space group  $C2/m$  with a monoclinic unit cell symmetry (Rayner 1974). The ideal chemical formula of phlogopite (and the isostructural biotite) is  $(\text{Mg, Fe})_6^{2+} [\text{Si}_6^{4+}, \text{Al}_2^{3+}] \text{K}_2^+ \text{O}_{20}^{2-} (\text{OH})_4^-$  where  $\text{Mg}^{2+}$  and  $\text{Fe}^{2+}$  generally fill the octahedral sites\*;  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  fill the tetrahedral sites,  $\text{K}^+$  are the inter-layer cations

\*An octahedron is formed of  $4\text{O}^{2-}$  and  $2\text{OH}^-$  and depending on the location of  $\text{OH}^-$  ions there are trans ( $M_1$ ) and cis ( $M_2$ ) sites; structurally there are four  $M_2$  and two  $M_1$  sites per unit cell.

and the remaining ones are octahedral and tetrahedral anions. Large variations in this composition are known to occur.

Häggsström *et al* (1969) in their work on a biotite and a synthetic annite, reasoning on the basis of structural site populations, attributed the more intense outer  $\text{Fe}^{2+}$  doublet to  $M_1$  and the other one to  $M_2$  site. Ingalls (1964) had shown that for a six coordinated iron site the lattice sum (dominant part for  $\text{Fe}^{3+}$  state) and valence (dominant part for  $\text{Fe}^{2+}$  state) contributions to EFG occur with opposite signs. These two inferences taken together suggest that for high spin  $\text{Fe}^{3+}$  state the doublet with larger quadrupole splitting ( $\Delta E$ ) should belong to  $M_1$  (structurally lower in population) site and the other one to  $M_2$  site. This is also supported by the lattice sum calculations on EFG (Berrett and Fitzsimmons 1967). Thus several workers (Häggsström *et al* 1969; Annersten 1974, 1975; Goodman 1976a; Chandra and Lokanathan 1977) have fitted the Mössbauer spectra of micas in terms of just two doublets each for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  coordinations and have attributed them to two structural sites  $M_1$  and  $M_2$ .

However, Goodman (1976b) and later Mineeva (1978) argued that since micas form a wide solid solution range, several types of defects in charges as against an ideal distribution can occur leading to varying environments at different crystallographic sites. Using known structural parameters in biotite and phlogopite\* (Donnay *et al* 1964; Rayner 1974), they performed lattice sum calculations under point charge approximation to obtain EFG at the two inequivalent sites for  $\text{Fe}^{3+}$  state taking a random distribution of defect charges at the neighbouring crystallographic locations. Both these studies showed that variation in the nature of defect charges leads to a variation in EFG at either site which is larger than the difference in EFG values for the two sites calculated by assuming ideal charge distributions. This implies that the Mössbauer doublet assignments in terms of structural sites  $M_1$  and  $M_2$  may not be unique. However, although Mineeva extended the calculations upto 50 Å to get a convergence below 1% level, the effect of defect charges in both the studies was considered only at adjacent sites. Also the distribution of ionic charges in the lattice in a perfect random manner will not be electrostatically favourable (Krzanowski and Newman 1972).

The present paper, an experimental study of the mica phlogopite and an attempt at a model calculation of EFG to fit the experimental data, is motivated to put the problem of doublet assignment in micas in perspective even though its success is limited. The specimen chosen for the experimental work contains iron mostly in  $\text{Fe}^{3+}$  form. The reason for this choice is that in  $\text{Fe}^{3+}$  coordinated sites, there are mainly the crystal field and the core polarization contributions to the EFG, thus reducing the complexity of the problem of interpretation. The Mössbauer parameters and the orientations of EFG at  $\text{Fe}^{3+}$  sites are reported and the results are discussed.

## 2. EFG calculations for $\text{Fe}^{3+}$ sites in phlogopite structure

At high spin  $\text{Fe}^{3+}$  sites the major contributions to EFG arise from the crystalline fields and the core polarization effects which are lumped into the Sternheimer anti-shielding factor ( $1-\gamma_\infty$ ) (May 1971). Distortions in the spherically symmetric  $3p$  shells of iron due to overlap from  $2s$  and  $2p$  shells of  $\text{O}^{2-}$  also provide some contri-

\*The two are isostructural with the difference of relative Mg:Fe concentration; their unit cell parameters differ slightly.

butions but they are equal for the two sites ( $M_1$  and  $M_2$ ) as shown by Mineeva (1978) in the case of biotite. Difference in EFG values at the two sites would thus arise only from the crystalline field contributions. Further, the crystalline field contributions to EFG arise from monopoles (point charges) as well as multipoles present in the lattice. Thus the procedure usually adopted in fitting the calculations to experimental EFG data is to treat point charges and polarizabilities of the ions as adjustable parameters. However, as was pointed out by Mineeva (1978), perhaps due to the low symmetry of the structure in micas, the lattice contribution to EFG due to monopoles alone is most significant in determining the EFG values. Our calculations in phlogopite support the same. For these reasons we have worked under the point charge approximation. Goodman (1976b), the other previous worker on this problem, has also used the same approach.

First the EFG components at the  $M_1$  and  $M_2$  sites of phlogopite (Rayner 1974) were calculated for the ideal structure employing integral point charges. A rectangular coordinate system was introduced in the monoclinic unit cell of phlogopite taking  $x$  and  $y$  axes to coincide with  $a$  and  $b$  axes of the unit cell and  $z$  axis to be normal to the  $ab$  plane. The EFG components  $V_{ij}$  arising from lattice contribution were calculated by direct summation over a sphere with radius  $r$  using relations (May 1971):

$$V_{ij} = \frac{\partial^2 v}{\partial x_i \partial x_j} = \sum_k q_k \left( \frac{3x_{ik} x_{jk}}{r_k^5} - \frac{\delta_{ij}}{r_k^3} \right)$$

and 
$$\Delta E = (1 - \gamma_\infty) e^2 Q V_{ZZ} \left( 1 + \frac{\eta^2}{3} \right)^{1/2},$$

where  $x_{ik}$  is the component ( $i = x, y, z$ ) of the radius vector  $r_k$  from the origin to the ion  $k$  having charge  $q_k$ .  $V_{ZZ}$  is the principal component obtained by diagonalizing the tensor  $V_{ij}$ ;  $Q$  is the quadrupole moment of  $^{57}\text{Fe}$  and  $\eta$  is the asymmetry parameter. A computer program was developed in Fortran IV language; the atomic positions and charges were fed for a unit cell and others were generated by raising the position coordinates by respective lattice constants. The calculations showed that in going from a  $r$  value of 10 Å to 30 Å the values of the EFG components change by as much as 18% and in further going to 50 Å the changes are less than 0.5%. Hence all other calculations were carried out only for  $r = 50$  Å.

As regards the effect of defect charges, Krzanowski and Newman (1972) made a critical analysis on the distribution of octahedral charges in the layered silicate lattice. Arguing that a random distribution of octahedral charges  $R^{2+}$ ,  $R^{3+}$  and vacancy ( $\square$ ) would also imply such combinations as would be disallowed by Pauling's electrostatic valence rule (Pauling 1960), they concluded that these arrange in such a way that the sum  $V$  of three adjoining octahedral cationic charges is in the range  $4 < V < 7$  or  $5 < V < 8$ . Also if more than 15% of iron is in  $\text{Fe}^{3+}$  state the defect charges ( $R^{3+}$  and  $\square$ ) generally arrange into chains of configurations resembling the letters  $Y$  or  $X$ . In the present calculations we have followed this procedure for the distribution of defects only for octahedral sites. All the  $+3e$  octahedral charges have been taken to be associated with  $\text{Fe}^{3+}$ . Retaining total octahedral cationic charge of  $+12e$  in an ideal unit cell (so that occurrence of  $\text{Fe}^{3+}$  correspondingly leads to  $\square$  in some octa-

hedral sites) and assuming  $\text{Fe}:\text{Mg}=1:2$  (typically observed in phlogopites) and  $\text{Fe}^{2+}:\text{Fe}^{3+}=1:9$  (high  $\text{Fe}^{3+}$ ), we get for the fractional populations:  $a(R^{2+})=0.6087$ ,  $b(R^{3+})=0.2609$ ,  $c(\square)=0.1304$ . The probability factors for different charge combinations at three adjoining octahedral sites were calculated using the expansion  $(a+b+c)^3$ . This procedure yields probabilities quite close to those obtained by computer simulation method (Krzanowski and Newman 1972). The charges  $R^{2+}$ ,  $R^{3+}$  and  $\square$  at octahedral sites in a unit cell were put in a way as to form  $Y$ -type combinations. The same is depicted in figure 1. For other combinations the charges were replaced by their appropriate counterparts. For example, in the case of the combination  $R^{2+} R^{2+} R^{3+}$ ,  $\square$  was replaced by  $R^{2+}$ . The effects from different  $Y$ -type combinations of octahedral cations were taken into account by summing their contributions with due weightage according to their probability of occurrence. Combinations below 3% probability level were neglected. Correspondingly the occurrence of the combination  $R^{3+} R^{3+} \square$  which would lead to a  $X$ -type distribution is negligible ( $\sim 3\%$ ) in the present case. Krzanowski and Newman (1972) also mentioned that the probability of  $X$ -chain formation is smaller than that of  $Y$ -chain formation.

Table 1 gives the calculated contributions from different ions in an ideal phlogopite structure. The contributions from different  $Y$ -chain combinations of octahedral cations are given in table 2. In table 3 are noted the diagonalized principal axes components as well as calculated  $\Delta E$  and  $\eta$  values; predictions using an ideal charge distributions and experimental  $\Delta E$  values are also included for the purpose of comparison. It is found that the calculated  $\Delta E$  values using a  $Y$ -chain distribution of octahedral defect charges are in good agreement with the experimental ones. The calculations yield a  $\sim 30\%$  smaller  $\Delta E$  for  $M_2$  than for  $M_1$  site as against a  $\sim 40\%$  difference observed experimentally. This implies that the assignments of the two observed  $\text{Fe}^{3+}$  doublets in micas to  $M_1$  and  $M_2$  sites are quite valid.

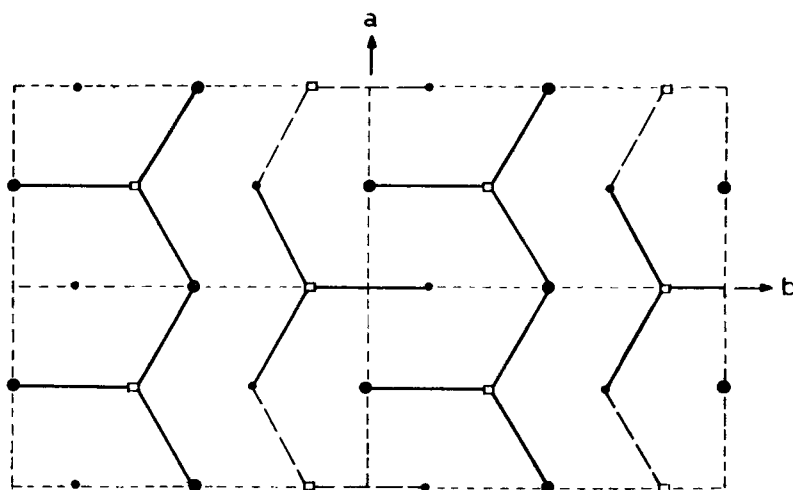


Figure 1. Octahedral cations projected on  $ab$  plane in phlogopite mica, ●:  $R^{3+}$ , •:  $R^{2+}$ , □: vacancy. Four adjoining unit cells separated by broken lines are shown. Solid lines depict chain type distributions.

**Table 1.** Lattice sum contributions ( $r=50\text{Å}$ ) to EFG tensors (non-diagonalized) in units of  $(1-\gamma_{\infty}) \cdot e \cdot 10^{24}$  at  $M_1$  and  $M_2$  sites from integral point charges at each species of ion in a phlogopite mica. In all the cases  $V_{xy}$  and  $V_{yz} < 10^{-3}$ .

Site	Contributing ion*	$V_{xx}$	$V_{xz}$	$V_{yy}$	$V_{zz}$
$M_1$	(Si, Al) <sup>+3.75</sup>	-0.3310	-0.1741	-0.1400	+0.4710
	(Fe, Mg) <sup>+2</sup>	+0.2732	-0.0010	+0.2868	-0.5599
	(O <sub>I</sub> , O <sub>II</sub> , O <sub>III</sub> ) <sup>-2</sup> , K <sup>+1</sup>	+0.4843	+0.5675	-0.5698	+0.0853
	(O <sup>-2</sup> , H <sup>+1</sup> )	-0.6397	-0.4062	+0.3160	+0.3236
	Total	-0.2132	-0.0138	-0.1070	+0.3200
$M_2$	(Si, Al) <sup>+3.75</sup>	-0.1876	+0.0865	+0.2837	+0.4713
	(Fe <sub>I</sub> , Fe <sub>II</sub> ) <sup>+2</sup>	+0.2826	-0.0010	+0.2771	-0.5598
	(O <sub>I</sub> , O <sub>II</sub> , O <sub>III</sub> ) <sup>-2</sup> , K <sup>+1</sup>	-0.3116	-0.2790	+0.2312	+0.0800
	(O <sup>-2</sup> , H <sup>+1</sup> )	+0.0856	+0.2034	-0.4086	+0.3228
	Total	-0.1310	+0.0099	+0.3834	+0.3143

\*Superscripts are integral point charges assigned to different ions; at the tetrahedral sites +3.75e charge was placed corresponding to an average occupancy of Si:Al=3:1.

**Table 2.** Lattice sum contribution ( $r=50\text{Å}$ ) to EGF tensors (non-diagonalized) in units of  $(1-\gamma_{\infty}) \cdot e \cdot 10^{24}$  at the  $M_1$  and  $M_2$  sites from different octahedral cation combinations of  $R^{2+}$ ,  $R^{3+}$ ,  $\square$  extending in Y-type chains throughout the entire lattice. In all the cases  $V_{xy}$  and  $V_{yz} < 10^{-5}$ .

Site	Y-distribution	$V_{xx}$	$V_{xz}$	$V_{yy}$	$V_{zz}$
$M_1$	$R^{2+} R^{2+} \square$	0.0249	-0.0001	0.0259	-0.0508
	$R^{2+} R^{3+} \square$	0.0239	-0.0001	0.0249	-0.0488
	$R^{2+} R^{2+} R^{2+}$	0.0680	-0.0002	0.0714	-0.1394
	$R^{2+} R^{2+} R^{3+}$	0.0934	-0.0004	0.0978	-0.1912
	$R^{3+} R^{3+} R^{2+}$	0.0478	-0.0002	0.0501	-0.0979
$M_2$	$R^{2+} R^{2+} \square$	0.0387	-0.0001	0.0378	-0.0764
	$R^{2+} R^{3+} \square$	0.0410	-0.0001	0.0407	-0.0817
	$R^{2+} R^{2+} R^{2+}$	0.0704	-0.0002	0.0690	-0.1394
	$R^{2+} R^{2+} R^{3+}$	0.1088	-0.0004	0.1081	-0.2170
	$R^{3+} R^{3+} R^{2+}$	0.0491	-0.0002	0.0488	-0.0979

**Table 3.** The principal EFG components in units of  $(1-\gamma_{\infty}) \cdot e \cdot 10^{24}$ , quadrupole splitting  $\Delta E$  in mm/sec and asymmetry parameter  $\eta$  at  $M_1$  and  $M_2$  sites in a phlogopite mica.  $(1-\gamma_{\infty})=10.14$ ,  $e=4.80325 \times 10^{-10}$  esu and  $Q=0.21$  b.

Site	Octahedral distribution type	$V_{XX}$	$V_{YY}$	$V_{ZZ}$	$\Delta E$	$\eta$
$M_1$	Y-chain	-0.1237	-0.2285	0.3522	1.14	0.30
	Ideal	-0.1065	-0.2137	0.3205	1.04	0.33
	Experimental	—	—	—	1.28	—
$M_2$	Y-chain	-0.1000	-0.1623	0.2623	0.85	0.24
	Ideal	-0.1312	-0.1834	0.3148	1.01	0.17
	Experimental	—	—	—	0.76	—

### 3. Experimental results and discussion

The experimental set-up for recording the Mössbauer spectra is the same as described elsewhere (Chandra and Lokanathan 1977). A thin (24 mg/cm<sup>2</sup>) uniform sheet of a phlogopite mica of 1.5 × 2.0 cm<sup>2</sup> size obtained from Andhra Pradesh (India) was chosen for study. It was characterized by x-ray diffractometry comparing the powder pattern with the standard ASTM cards. Mössbauer spectra were recorded for different orientations of the sheet with the  $\gamma$ -ray being directed at  $\theta$  angles of 0, 15°, 30°, 45°, 60° and 70° with the normal ( $c^*$  axis) to the plane of the sheet. The source subtended 7° half-cone angle at the detector.

All the spectra have been computer resolved using a standard program (Meerwall 1975). Good  $\chi^2$  values were obtained for a fit into three doublets—two corresponding to Fe<sup>3+</sup> and one to Fe<sup>2+</sup> state\*\*. As a typical example computer resolved spectrum for  $\theta=60^\circ$  is shown in figure 2. The Mössbauer site population for Fe<sup>2+</sup> state is small (~17%) and we could not resolve two doublets corresponding to  $M_1$  and  $M_2$  sites separately. The isomer shift (IS) values with respect to natural iron are 0.36 (1), 0.35 (1) and 1.09 (1) (all in mms<sup>-1</sup>) for Fe<sup>3+</sup> ( $M_1$ ), Fe<sup>3+</sup> ( $M_2$ ) and the Fe<sup>2+</sup> doublets respectively. These are all characteristic of high spin states. The ratio of site population for the outer Fe<sup>2+</sup> doublet to the inner one is ~1:2;  $\Delta E$  of the outer doublet is ~40% larger. Following the line of arguments discussed in § 1 and our calculations (*cf.* § 2), the outer Fe<sup>2+</sup> doublet (weaker one) is attributed to  $M_1$  and the inner Fe<sup>3+</sup> doublet (stronger one) to  $M_2$  site.

Large variations in the intensity of the two halves of a quadrupole doublet spectra were observed at different angles (between  $\gamma$ -ray and the sheet normal  $c^*$ ). This is clearly demonstrated in figure 3 where the experimental spectra at  $\theta=0, 30^\circ$  and  $70^\circ$  are shown. The doublet intensity ratios  $R$  ( $I_{\text{high energy}}/I_{\text{low energy}}$ ) as obtained from computer analyses of the spectra are plotted as a function of  $\theta$  in figures 4a and 4b for  $M_1$  and  $M_2$  sites. Although the variation in the case of  $M_2$  site is not as regular and sharp as in the case of  $M_1$  site, the general trend in both the cases is one of  $R$  decreasing with increasing  $\theta$ . This would indicate positive quadrupole coupling const-

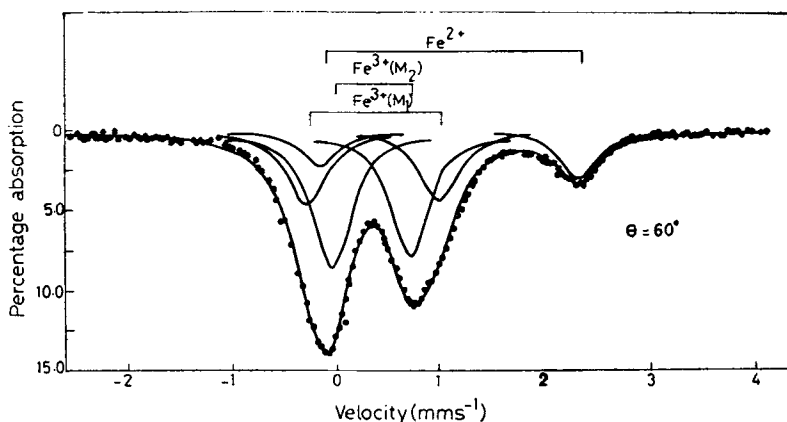


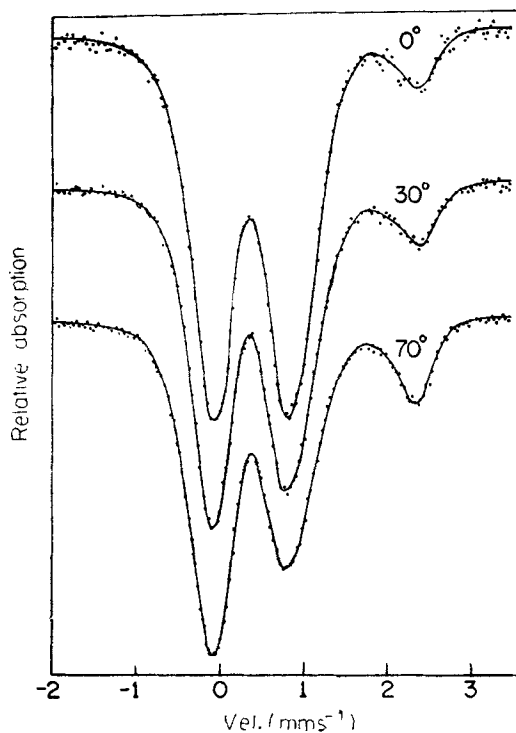
Figure 2. Mössbauer spectrum of a phlogopite mica sheet oriented at  $\theta=60^\circ$  with respect to  $\gamma$ -ray. Computer resolved lines are also shown.

\*\*Line widths (full width at half maximum) for two Fe<sup>3+</sup> doublets were constrained to be equal. In going from one  $\theta$  to another these changed from 0.454(4) to 0.479(18) mms<sup>-1</sup>.

ants for both the sites. For  $\text{Fe}^{2+}$  octahedral sites in the isostructural mica biotite the coupling constant is reported negative (Chandra and Lokanathan 1977). Thus our studies on  $\text{Fe}^{3+}$ s tate agree with Ingalls (1964) prediction of opposite signs of the coupling constants for the two oxidation states of iron. Annersten (1975) also inferred opposite signs for the coupling constant at  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  sites based on his studies of powdered biotite at different orientations but its absolute sign for either of the states was not reported. Further in order to estimate the angle  $\alpha$  between  $V_{ZZ}$  and the sheet normal  $c^*$  we have used the approximate relations<sup>†</sup> developed by Chandra and Lokanathan (1977). In figures 4a and 4b along with the experimental  $R$  values are also plotted the model predictions against  $\theta$  for different  $\alpha$  values. It is seen that one may put a limit  $30^\circ < \alpha < 40^\circ$  for  $M_1$  site. For the  $M_2$  site the predictions and the experimental points do not match well but one may still put a limit of  $40^\circ < \alpha < 50^\circ$ . If  $\eta$  takes a large value ( $\sim 0.5$ ), the angles  $\alpha$  for the two sites will reduce by about  $5^\circ$ .

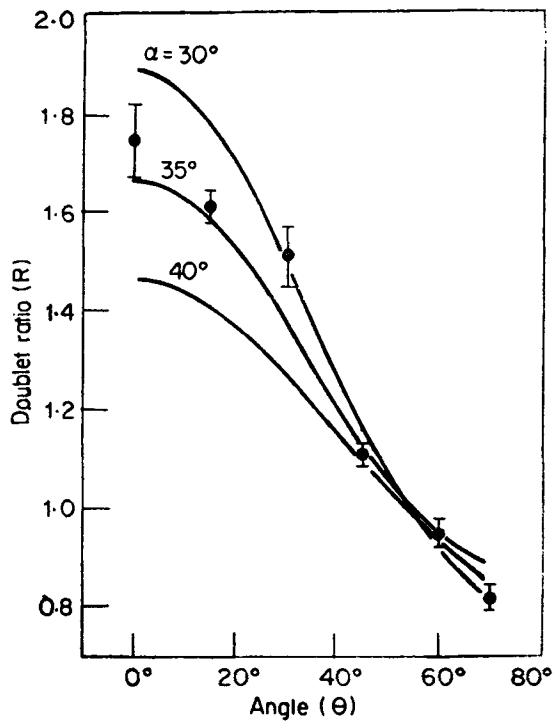
#### 4. Comparison between theoretical predictions and experimental results

Among the various parameters, as mentioned earlier, there is good agreement between the observed values of  $\Delta E$  and model predictions and the positive sign of

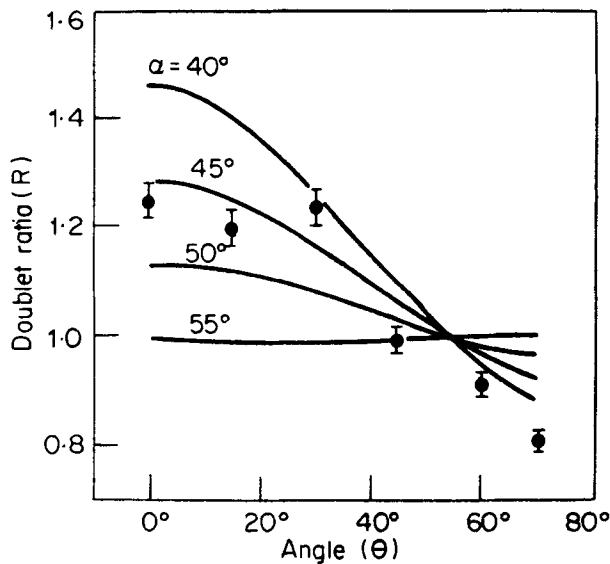


**Figure 3.** Mössbauer spectra of a phlogopite mica sheet oriented at  $\theta=0, 30^\circ$  and  $70^\circ$  with respect to  $\gamma$ -ray.

<sup>†</sup>The approximations involved in these expressions are justified in the present case. Spectra recorded at four different azimuth orientations in the mica plane, viz.  $\phi$  (arbitrary)= $0, 30^\circ, 60^\circ$  and  $90^\circ$  keeping  $\theta=30^\circ$  (fixed), are all identical implying the two crystallographic axes to be randomly distributed in the  $ab$  plane. This could also result from the presence of polytypes (Ross *et al* 1966). Further our calculations show  $\eta \sim 0.30$  and as the present procedure is not capable of resolving  $\eta$  values in the range  $\eta=0$  and  $0.5$ , we have assumed  $\eta=0$ .



(a)



(b)

**Figure 4.** Doublet intensity ratios  $R = I_{\text{high energy}}/I_{\text{low energy}}$  for a phlogopite mica sheet versus the orientation angle  $\theta$  between  $\gamma$ -ray and normal to the sheet for (a)  $M_1$  (trans) site and (b)  $M_2$  (cis) site. The solid curves are theoretical plots as a function of EFG principal axis orientation.



quadrupole coupling constant ( $Q$  being positive) for both the  $\text{Fe}^{3+}$  doublets. Regarding the asymmetry parameter  $\eta$  the present experiment is not capable of its determination and hence an examination of the correctness of the model prediction on  $\eta$  is not possible. However, the model fails to predict the EFG orientation. While the predictions are  $\alpha < 5^\circ$  for both the sites, the experimental values are  $\alpha \sim 30^\circ - 50^\circ$ . It should be noticed that as for octahedral cations, charge variations ( $\square$ , etc.) and their regular distribution may also occur for other ions in the lattice. Also in actual situations the effective charges will assume other than integral values. For example, placing a charge  $-1.6e$  on oxygens instead of  $-2e$  shifts  $\alpha \rightarrow 8^\circ$ . It seems unlikely, however, that this alone would be sufficient to reproduce the large  $\alpha$  experimentally observed. The present work, however, does show that an ordered arrangement of octahedral cations is able to reproduce the quadrupole splitting at both the octahedral sites suggesting that the cations do not distribute in a random manner and also that the Mössbauer doublet assignments in terms of  $M_1$  and  $M_2$  structural sites are quite valid.

### Acknowledgement

One of the authors (AK) is grateful to the Department of Atomic Energy, India for the award of a fellowship.

### References

- Annersten H 1974 *Am. Miner.* **59** 143  
Annersten H 1975 *Fortschr. Miner.* **52** 583  
Ballet O, Coey J M D and Messenet O 1979 *J. Phys. (Paris) Colloq.* **C-2** 40 283  
Berrett R R and Fitzsimmons B W 1967 *J. Chem. Soc. (A)* 525  
Chandra R and Lokanathan S 1977 *Phys. Status Solidi* **B83** 273  
Donnay G, Morimoto N, Takeda H and Donnay J M D 1964 *Acta Crystallogr.* **17** 1369  
Goodman B A 1976a *Mineral. Mag.* **40** 513  
Goodman B A 1976b *J. Phys.* **37** C6-819  
Hägström L, Wappling R and Annersten H 1969 *Chem. Phys. Lett.* **4** 107  
Helsen J A, Van Deyck M, Langouche G, Goussement R, Van Rossum M and Schmidt K P 1975 *Clays and Clay Miner.* **23** 332  
Ingalls R 1964 *Phys. Rev.* **A133** 787  
Krzanowski W J and Newman A C D 1972 *Mineral. Mag.* **38** 926  
May L 1971 *An introduction to Mössbauer spectroscopy* (New York: Plenum Press)  
Meerwall Von E 1975 *Computer Phys. Commun.* **9** 117  
Mineeva R M 1978 *Phys. Chem. Miner.* **2** 267  
Pauling L 1960 *The nature of the chemical bond* (Ithaca: Cornell University Press) p. 548  
Rayner J H 1974 *Mineral. Mag.* **39** 850  
Ross M, Takeda H and Wones D R 1966 *Science* **151** 191  
Zory P 1965 *Phys. Rev.* **A140** 1401