A high-temperature Fourier transform infrared study of the interlayer and Si-O-stretching region in phengite- $2M_1$

M. MOOKHERJEE^{1,*} AND S. A. T. REDFERN^{1,2}

¹ Department of Earth Sciences, University of Cambridge, Downing St., Cambridge CB2 3EQ, UK, and ² R.S.E.S, Australian National University, Mills Road, Canberra ACT 0200, Australia

(Received 22 June 2001; revised 10 October 2001)

ABSTRACT: A natural phengite- $2M_1$ of composition (K_{0.95}Na_{0.05})(Al_{0.76}Fe_{0.14}Mg_{0.10})₂ (Si_{3.25}Al_{0.75})O₁₀(OH_{1.96}F_{0.04}) [a = 5.2173(1) Å, b = 9.0493(2) Å, c = 19.989 (1) Å and $\beta = 95.734(4)^\circ$] was studied using *in situ* high-temperature FTIR. Correlations to structural changes were made using previously-reported neutron diffraction data from the same sample. Correlations have been made between the microscopic atomic displacements (arising from thermal effects) and analogous macroscopic properties, such as bond strain and ditrigonal distortions. Spectra were collected in the far-infrared region to study the behaviour of the interlayer (K⁺) cation and also in the mid-infrared region to distinguish the Si–O stretching modes. We found anisotropic thermal expansion of the interlayer site. The K–O bond length is divided into K–O_{outer} and K–O_{inner}, and the K–O_{inner} bond length is correlated with the far-infrared spectra. The thermal dependence of the correlation between K–O bond length and corresponding far-infrared stretching frequency is different from the effect of the chemical composition. We also found that the K–O bond strain could be successfully resolved into the sum of inner strain and lattice strain. The Si–O stretching mode, obtained from the mid-infrared measurements, showed only weak changes. However, the neutron refinement data showed different thermal behaviour for distinct crystallographi c *T*-sites.

KEYWORDS: phengite- $2M_1$, FTIR, lattice and inner deformation.

Infrared (IR) absorption spectra of phengite in the far-infrared region have been reported by Ishii *et al.* (1967), Tateyama *et al.* (1977), Velde & Couty (1985), Prost & Laperche (1990) and Schroeder (1990, 1992). The region between 60 and 120 cm⁻¹ shows absorption bands, which are often attributed to the presence of an interlayer cation (K⁺). These bands are absent in IR spectra of pyrophyllite and talc, which do not have interlayer cations (Tateyama *et al.*, 1977). In phengite, the interlayer cation has six O atoms forming ditrigonal rings on the adjacent sides of the interlayer. Of the twelve nearest O atoms, six (three above and three below)

* E-mail: mm329@cam.ac.uk DOI: 10.1180/000985502372003 6 are located closer to the interlayer cation (K^{+}) than the other six. However, the effective coordination number (ECoN) of the interlayer site depends on the amount of ditrigonal distortion, and their correlation is already well established. Tainiolite and annite display a high ECoN (11.9-12.0), biotites, phlogopites and lepidolites display a medium ECoN (9.0-10.0), muscovites have lower ECoN values (8.0-9.0) and paragonites have the lowest ECoN (6.0) (Weiss et al., 1992). The K-O bond lengths can thus be divided into K-O_{inner} and K-Oouter (Tateyama et al., 1977). The IR bands in the region $85-115 \text{ cm}^{-1}$ were attributed to K–O stretching vibrations by Ishii et al. (1967) and were used to calculate K-O bond lengths in micas (Tateyama et al., 1977). Velde & Couty (1985), however, were doubtful about assigning the bands

in the regions $50-112 \text{ cm}^{-1}$ and $118-145 \text{ cm}^{-1}$ solely to the interlayer ion movements. They invoked the idea of "silica polymer" vibration, which they suggested was the major contributor to the far-infrared (FIR) spectrum for layer silicates such as illites. They suggested that the interlayer cation, being bounded not only by the "silica polymer" network O atoms but also by the O atoms of the two layers of H₂O molecules, seems to have little influence on the bands at 97 cm⁻¹ and 138 cm^{-1} which they claim show little variation between different layer silicates. More recently, however, Schroeder (1990, 1992), confirmed that FIR absorption measurements of the interlayer mode frequency can be employed as a proxy for the K-O bond distance. A detailed characterization and assignment of the FIR region is reported by Diaz et al. (2000). To assign absorption bands due to K⁺ in muscovite, they performed dichroic experiments. A muscovite crystal was rotated about the crystallographic axis, c*, a, or b. Two bands corresponding to the vibration modes of K⁺ appeared at 107 and 110 cm⁻¹ (rotation about c^*), 107 and 143 cm⁻¹ (rotation about a) and 110 and 143 cm⁻¹ (rotation about b), respectively. Midinfrared (MIR) absorption in the region of 960-1150 cm⁻¹ was reported by Farmer & Russell (1964) and Ishii et al. (1967) amongst others.

Of course the chemical compositions of micas vary widely (Tischendorf et al., 2001). Depending on the chemical composition of the layer silicate, the absorption bands at 1019 cm⁻¹ (for talc, Ishii et al., 1967), 1120, 1107, 1034 and 1003 cm⁻¹ (for dickite), 1120, 1080, 1048 and 1025 cm⁻¹ (for Wyoming montmorillonite), 1117, 1074, 1038 and 1010 cm⁻¹ (Woburn montmorillonite), 1091 ,1034 and 1017 cm⁻¹ (for nontronite) (Farmer & Russell, 1964) are assigned to Si-O stretching modes. Using ideal hexagonal symmetry (i.e. ignoring the distortion of the Si tetrahedra about the vertical axes parallel to the sheet, so that the apical O atoms, Oapical, do not lie immediately under Si atoms) with a point group symmetry of C_{2v} , Farmer & Russell (1964) described the modes as a₁ (which develops a dipole perpendicular to the sheet), b₁ and b₂ (developing dipole moments in the plane of the sheet perpendicular to each other), and a₂ which develops no dipole and is IR inactive (Fig. 1). However, in reality, the actual vibrations involve linear combinations of the forms described by Farmer & Russell (1964).

The purpose of the present paper is to report: (1) the behaviour of the (K^+) cations in the interlayer regions, its relationship with the ditrigonal distortions and microsopic displacements of the basal oxygen atoms; and (2) the behaviour of the TO_4 tetrahedra, particularly the displacement of the tetrahedral cation away from the plane of basal oxygen and Si-O_{apical} stretching vibrational modes. Neutron diffraction provides a powerful structural adjunct to FTIR studies of micas (e.g. Pavese et al., 2000). Here we use both in situ high-temperature FTIR and crystallographic data from refinement of the neutron diffraction experiments previously reported in Mookherjee et al. (2001) to shed light on the behaviour of the interlayer and basal oxygens of mica.

MATERIAL AND METHODS

A natural phengite- $2M_1$ sample from Livadi, Greece, of compositon ($K_{0.95}Na_{0.05}$) ($Al_{0.76}Fe_{0.14}Mg_{0.10}$)₂($Si_{3.25}Al_{0.75}$)O₁₀ (OH_{1.96}F_{0.04}) (C2/c) was used for neutron diffraction study as outlined by Mookherjee *et al.* (2001). The same sample was used for the *in situ* high-temperature IR spectroscopic measurements in the FIR and MIR regions.

Two types of pellets (spread thinly onto a silicon wafer) were used for different frequency ranges (Table 1). For the FIR region the sample was heated (from 300 to 610 K). For the MIR region, the sample was heated (from 300 to 460 K) and transmission spectra were recorded using KBr pellets.

The spectra were recorded under vacuum using a Brucker 113V FT-IR spectrometer. For sample heating, the specimen was positioned within a cylindrically-wound platinum resistance furnace. The temperature was measured using a Pt/Pt-Rh thermocouple, which was pressed against the sample. The temperature stability was better than ± 1 K and a heating rate of 15 K/min was used. During the heating sequences, samples were held at each temperature for at least 15 min to allow thermal equilibration before commencing the IR data collection.

The resolution of the 113V instrument was set to 2 cm^{-1} for MIR and 4 cm^{-1} for FIR. The spectrum was calculated by Fourier transformation of 350 interferometer scans. All spectra were then recorded as absorbance α , with $\alpha = -\log_{10}(I_{\text{sample}}/I_{\text{reference}})$, where *I* is the single-beam transmission intensity.



FIG. 1. (a) A section of a single ditrigonal ring formed by the TO_4 polyhedra perpendicular to the z^* direction (at 373 K). The interlayer K/Na (not shown, for clarity) sits at similar *x*,*y* position coordinates as those of the hydroxyl group (O(3)–H(1)) in the figure. The octahedral cations are omitted for clarity. Apical oxygen atoms, labelled O(1) and O(2) are part of T(1) and T(2) respectively and those labelled O(4), O(5) and O(6) are basal oxygen atoms. O(3) is the part of the hydroxyl group and is roughly at the centre of the ring and at the same *z* coordinate as that of the O(1) and O(2) atoms (Mookherjee *et al.*, 2001). (b) A view of two ditrigonal rings viewed perpendicular to (a). Structures are from refinements of neutron data collected at 373 K (Mookherjee *et al.*, 2001). (c) Si–O stretching vibration mode a_1^1 (Farmer & Russell, 1964). (d) Si–O stretching vibration mode a_2^1 (Farmer & Russell, 1964).

TABLE 1. Experimental details for the various IR absorption experiments.

Matrix	PW (mg)	AS (mg)	IR region (cm ⁻¹)	Source	Detector	Beam splitter	T region (K)
Silicon wafer	~100	~2 - 3	70 - 350	Hg-arc	DTGS	Mylar 6 µm	300 - 610
KBr	200	0.50	800 - 1200	Globar	MCT	KBr	300 - 460

PW = pellet weight; AS = amount of sample; *T* region = temperature region; DTGS = room temperature DTGS detector; MCT = liquid nitrogen-cooled MCT detector; the silicon wafer was 0.5 mm thick with both sides polished.

Profile analysis of the spectra was achieved by fitting Lorentzian peak profiles to the recorded absorption spectra using the program OPUS (software package from Bruker).

RESULTS AND DISCUSSION

Among the geometric crystallographic parameters which are generally used to describe the topology of micas (Bailey, 1984; Brigatti & Guggenheim, 2000) we consider: (1) the tetrahedral flattening angle,

$$\tau = \sum_{i=1}^{3} (\overline{\mathrm{O}_{\mathrm{apical}} - T - \mathrm{O}_{\mathrm{basal}}})/3;$$

(2) the tetrahedral rotation/ditrigonal distortion angle, $\alpha = \frac{1}{2}(120 - \phi_i)$, where ϕ_i is the angle between basal edges of neighbouring tetrahedral atoms articulated in the ring; and (3) the displacement of the tetrahedral cations from their ideal position, $T_{\rm disp}$ (Å)

$$=\sqrt{\left(\langle T - O_{\text{basal}} \rangle\right)^2 - \frac{\langle O - O \rangle_{\text{basal}}\right)^2}{3}} - \frac{(T - O)_{\text{apical}}}{3}$$

These parameters provide information about the atomic-scale adjustments as a result of changes in temperature, pressure or chemical composition.

Interlayer region

To characterize the behaviour of the interlayer cation, spectra were collected in the region from 60 to 300 cm⁻¹ (Fig. 2). The spectra were collected at temperatures between 300 and 610 K in 20 K steps up to 600 K and with a final spectrum taken at 610 K. The absorption feature at ~100 cm⁻¹ was



FIG. 2. Thermal evolution of IR powder spectra due to K-O_{inner} stretching absorption. Inset shows the difference in the spectra at 300 and 610 K.

fitted with two Lorentzian profiles, and the temperature evolution of the two peaks is shown in Fig. 3. The peak at ~105 cm⁻¹ (300 K) decreases to $\sim 102 \text{ cm}^{-1}$ (610 K) with 2.4% change in the mode frequency, whereas the peak at $\sim 94 \text{ cm}^{-1}$ does not show any significant variation with temperature. The third peak, located at ~140 cm⁻¹, hardly shows any variation with temperature. The three peaks at ~94, 105 and 140 cm⁻¹, are probably due to the transition moments parallel to the b, a and c^* directions (corresponding to ~107, 110 and 143 cm⁻¹, Diaz et al., 2000). In comparison with the single crystal dichroic experiment of Diaz et al. (2000), we found all the three bands together, since we used a powder sample. The local environment of the K⁺ ion shows that the coordinating oxygen ions (belonging to the ~12 coordination) are approximately related by a $C_{3i}(\bar{3})$ axis of symmetry parallel to c^* axis with the K⁺ ion on the inversion centre. The space group of phengite- $2M_1$, however, is C1 2/c, which can be thought of as consisting of two primitive unit cells (P) with a point group C_{2h} (2/m). The (P) cell contains two K⁺ ions, which lie on C_2 (2-fold) axis, parallel to the b axis.

Hence, considering the local environment (with exact symmetry C_{3i} (3)), vibrations due to K⁺ would have been doubly degenerate perpendicular to c^* (in the (001) plane) with an additional out-of-plane (001) vibration parallel to c^* . In reality the degeneracy is lost. The two in-plane peaks resulting from loss of degeneracy are at 94 cm⁻¹ (which is a vibrational mode with symmetry corresponding to the singly degenerate even representation A_u and

wavevector parallel to b) and at 105 cm⁻¹ (which is a vibrational mode with symmetry corresponding to the singly degenerate even representation B_u and wavevector parallel to a). The vibration at ~140 cm⁻¹ is also a B_u type parallel to c^* .

The marked difference in the frequency of the inplane and out-of-plane vibration is not an indication of strong force constant for the out-of-plane vibration (with higher frequency). For IR observation involving thin flaky crystal structure (thin in one dimension compared to other two) out-of-plane absorption is observed at a frequency corresponding to the longitudinal vibrational mode of the crystals. When a strong dipole oscillation is created by vibration, this longitudinal frequency is substantially larger than the corresponding transverse mode (Diaz et al., 2000). The in-plane vibrations of thin sheets are observed at the transverse mode frequency (Farmer and Russell, 1966) and may account for the observed difference in the frequency.

From *in situ* high-temperature neutron diffraction data (Mookherjee *et al.*, 2001), we found that the thermal expansivities of three short bonds were:

$$\begin{array}{l} \alpha_{<\rm K-O6'>} = 1.33 \times 10^{-5} \ \rm K^{-1}, \\ \alpha_{<\rm K-O5'>} = 9.0 \times 10^{-5} \ \rm K^{-1}, \\ \alpha_{<\rm K-O4'>} = 4.56 \times 10^{-5} \ \rm K^{-1} \end{array}$$

and those of three longer bonds are:

 $\alpha_{<K-O4>} = -2.58 \times 10^{-5} \text{ K}^{-1},$ $\alpha_{<K-O5>} = -2.95 \times 10^{-5} \text{ K}^{-1},$ and $\alpha_{<K-O6>} = 0.572 \times 10^{-5} \text{ K}^{-1}$ (in the range 293–973 K).



FIG. 3. Temperature variation of the fitted peak (represented by open squares) showing slight decrease in frequency, from 105 cm⁻¹ at 300 K to 102 cm⁻¹ at 610 K. The other peak (represented by open circles) does not show significant variation.



FIG. 4. Variation of K-O_{inner} [K-O4'; K-O5' and K-O6'] bond length with temperature.

The temperature evolution of the three short bonds, i.e. K-O4', K-O5' and K-O6' is shown in Fig. 4. Because the temperature intervals for the neutron diffraction study and IR study are different, we have interpolated the average values of the K-O_{inner} bond corresponding to the same temperature intervals as that of the IR study. In Fig. 5, the frequencies of the K-Oinner bond-stretching modes are plotted against the corresponding K-Oinner bond length (for different temperatures) from our experimental data. The plot derived by Tateyama et al. (1977) for the average K-O_{inner} bond length and the corresponding IR absorption frequency for layer silicates of widely varying composition (including both dioctahedral and trioctahedral structures) is also shown for comparison (Table 2). The result for the phengite reported here lies between that for muscovite and phengite samples reported by Tateyama *et al.* (1977). The influence of temperature on the $K-O_{inner}$ bond length and K-Ostretching frequency is clearly not identical to the influence of chemical composition. This probably reflects a difference between trioctahedral and dioctahedral micas.

Inner elasticity

The crystal structure deformation caused by a thermal effect can be analysed in a similar fashion to that produced by mechanical stress (Catti, 1989). In comparison to the mechanical stress having six independent components, thermal strain has only one variable parameter, the temperature.

In the following section we develop and elucidate the formalism originally introduced by Catti (1989), to understand the strain within a crystal structure. It is



FIG. 5. Relationship between K-O_{inner} bond length and stretching frequency. A comparison has been made between the previous data set (from Tateyama *et al.*, 1977) and the data from this work (Table 2).

Specimen		K–O _{inner} distances (Å)	K-O _{inner} stretching frequency (cm ⁻¹)
1 muscovite		2.855	108
2 muscovite		2.857	108
3 phengite		2.970	96
4 lepidoloite		2.980	95
5 lepidoloite		2.976	95
6 Li-phlogopite		2.995	90
7 phlogopite		2.970	90
8 phlogopite		2.969	90
9 phlogopite		2.965	90
10 F- phlogopite		3.006	90
11 F- phlogopite		2.987	90
12 polilithinionite		3.000	90
13 Mg(IV) mica		3.061	86
14 annite		3.144	71
15 Fe-biotite		3.135	71
16 phengite (this study) 300 K	2.925	104.6
17 "	320 K	2.929	104.7
18 "	340 K	2.933	104.5
19 "	360 K	2.937	103.9
20 "	380 K	2.941	104.2
21 "	400 K	2.945	103.7
22 "	420 K	2.949	104.4
23 "	440 K	2.953	104.2
24 "	460 K	2.957	104.1
25 "	480 K	2.961	104.5
26 "	500 K	2.965	103.9
27 "	520 K	2.969	103.8
28 "	540 K	2.973	102.9
29 "	560 K	2.977	102.6
30 "	580 K	2.981	103.2
31 "	600 K	2.985	102.9
32 "	610 K	2.987	101.9

TABLE 2. FIR absorption frequencies and corresponding K-O_{inner} bond lengths (Å) for different sheet silicates.

1 – Güven (1971); 2 – Rothbauer (1971); 3 – Güven (1971); 4 – Takeda *et al.* (1971); 5 – Sartori *et al.* (1973); 6 – Takeda and Donnay (1966); 7 – Joswig (1972); 8 – Hazen and Burnham (1973); 9 – Rayner (1974); 10 – McCauley *et al.* (1073); 11 – Takeda and Morison (1975); 12 – Takeda and Burnham (1969); 13 – Tateyama *et al.* (1974); 14 – Hazen and Burnham (1973); 15 – Tepkin *et al.* (1969) and from 16–32 – the IR stretching frequencies are from the present work and corresponding bond length are obtained from the previously-reported neutron refinement of the same sample (Mookherjee *et al.*, 2001)).

well known that when a crystal is subjected to an homogeneous elastic stress, the induced deformation preserves translational symmetry and can be considered as the superposition of a pure lattice (external) strain and an internal strain (Born & Huang, 1954). The external strain describes the change in the lattice parameters. The internal strain describes the change in the fractional coordinates of atoms.

Formalism

The square of the distances between two atoms can be expressed in terms of X^TGX where G is the metric matrix (the determinant of which gives the square of the unit-cell volume) and X represents the fractional coordinates of the atom in consideration (see Appendix). The strain used to express larger deformation is the finite Lagrangian strain tensor (η). It can be expressed in terms of the change in the metric tensor or deformation (G' - G) as given by $\eta = \frac{1}{2}R^{T}(G' - G)R$ (Catti, 1985) where R relates the fractional coordinates and Cartesian coordinates of a point in the crystal before the deformation by the relation $X_i = R^{-1}x_i$. This tensor does not take account of the inner strain due to the relaxation of the atoms required to minimize the internal energy. In order to account for this inner deformation, we adopt the approach outlined below.

Let the separation between the two atoms at temperature θ_1 be denoted by d_{ii}

where
$$d_{ij}^2 = (x_i - x_j)^T G(x_i - x_j)$$
,

at higher temperature θ_2 be d_{ij}

where
$$d_{ij}^{'2} = (x_i' - x_j')^T G'(x_i' - x_j^i)$$
 (Fig 6).

Hence, the differences in the squares of the distance are given by

$$d_{ij}^{'2} - d_{ij}^2 = \{ (x_i' - x_j')^T G'(x_i' - x_j') \} - \{ (x_i - x_j)^T G(x_i - x_j) \}.$$

Figure 6 demonstrates that $x_i' = x_i + \Delta x_i$ and $x_j' = x_j + \Delta x_i$. Hence, substituting them in the difference

equation we get

$$\begin{aligned} &d_{ij}^{'2} - d_{ij}^{2} = \{(x_{i} + \Delta x_{i} - (x_{j} + \Delta x_{j}))^{T}G'(x_{i} + \Delta x_{i} - (x_{j} + \Delta x_{j}))\} - \{(x_{i} - x_{j})^{T}G(x_{i} - x_{j})\} = \\ &[\{(x_{i} - x_{j})^{T}G'(x_{i} - x_{j})\} - \{(x_{i} - x_{j})^{T}G(x_{i} - x_{j})\}] + \\ &[(\Delta x_{i} - \Delta x_{j})^{T}G'(x_{i} - x_{j}) + (\Delta x_{i} - \Delta x_{j})^{T}G'(\Delta x_{i} - \Delta x_{j})] + \\ &(\Delta x_{i} - \Delta x_{j})^{T}G'(\Delta x_{i} - \Delta x_{j}) + (x_{i} - x_{j})^{T}G'(\Delta x_{i} - \Delta x_{j})] \end{aligned}$$

The terms are arranged into two parts in square brackets. The term within the first square bracket can be further reduced to

$$\begin{aligned} &d_{ij}^{'2} - d_{ij}^{2} = [\{(x_{i} - x_{j})^{T} \Delta G(x_{i} - x_{j})\}] + \\ &[(\Delta x_{i} - \Delta x_{j})^{T} G'(x_{i} - x_{j}) + \\ &(\Delta x_{i} - \Delta x_{j})^{T} G'(\Delta x_{i} - \Delta x_{j}) + (x_{i} - x_{j})^{T} G'(\Delta x_{i} - \Delta x_{j})] \end{aligned}$$

The first term represents the pure lattice deformation, without any changes in the fractional coordinates, whereas the ΔG term represents only volume change. The second term however deals entirely with the changes in the fractional coordinates.

Thus we have been able to split the strain terms into the external strain, which varies the unit-cell lattice geometry only leaving the fractional coordinates of the atoms unchanged, and the inner strain, which varies the fractional coordinates. The



FIG. 6. The thermal strain experienced by the K–O bond. The low temperature (θ 1) bond length is denoted by d_{K-O} , and the high-temperature (θ 2) bond length is denoted by $d_{K-O'}$. The fractional coordinates of the O and K atom at temperature θ 1 are given by x_O and x_K respectively, where as at higher temperature θ 2 they are represented as x'_O and x'_K , respectively, with respect to a common origin O. (Note: this figure particularly shows K–O_{inner} bonds with positive coefficient of thermal expansion, for a negative thermal expansion the higher temperature (θ 2) bond length $d_{K-O'}$ would appear shorter.)

TABLE 3. Bond lengths, changes of squared bond lengths $\Delta (= d_{ij}^{'2} - d_{ij}^{2})$, (I) their lattice components, and (II) the component of inner deformation are reported for K–O bonds.

Catti et d	al. (1989)					
	Bond length (Å) at 373 K	Bond length (Å) at 973 K	$\stackrel{\Delta}{(A^2)}$	Ι	Π	α
K-04'	2.832(2)	2.942(5)	0.64	0.15	0.49	$6.47 \times 10^{-5} \text{ K}^{-1}$
K-04	3.303(2)	3.276(5)	-0.43	0.23	-0.66	$-1.36 \times 10^{-5} \text{ K}^{-1}$
K-05'	2.870(2)	3.002(4)	0.78	0.16	0.62	$7.67 \times 10^{-5} \text{ K}^{-1}$
K-05	3.528(2)	3.464(4)	-0. 43	0.23	-0.66	$-3.02 \times 10^{-5} \text{ K}^{-1}$
K-06'	2.843(2)	2.966(4)	0.71	0.15	0.56	$7.21 \times 10^{-5} \text{ K}^{-1}$
K-06	3.288(2)	3.256(4)	-0.21	0.19	-0.40	$-1.62 \times 10^{-5} \text{ K}^{-1}$
Data froi	m the present study					
	373 K	973K	Δ	Ι	II	α
K-04'	2.927(2)	2.998(2)	0.42	0.08	0.34	$4.56 \times 10^{-5} \text{ K}^{-1}$
K-04	3.217(2)	3.165(2)	-0.33	0.09	-0.43	$-2.58 \times 10^{-5} \text{ K}^{-1}$
K-05'	2.961(2)	3.118(2)	0.95	0.11	0.85	$9.0 \times 10^{-5} \text{ K}^{-1}$
K-05	3.396(2)	3.317(2)	-0.53	0.13	-0.66	$-2.95 \times 10^{-5} \text{ K}^{-1}$
K-06'	3.202(2)	3.228(2)	0.17	0.11	0.06	$1.33 \times 10^{-5} \text{ K}^{-1}$
K-06	2.914(2)	2.921(2)	0.04	0.09	-0.06	$0.572 \times 10^{-5} \text{ K}^{-1}$

Data source for the fractional position coordinates and corresponding lattice parameters: Mookherjee *et al.*, 2001. (Note, in Catti *et al.* (1989), the basal oxygens are labelled as O(1), O(2) and O(3); for ease of comparison they have been relabelled here as O(4), O(5) and O(6) respectively). α is the linear thermal expansion of each band.

individual atoms respond to the external strain: they tend to relax their position and minimize the total energy of the system. The inner strain generally occurs as a relaxation of the atomic positions to minimize the energy of the deformed lattice, and hence it is a function of the lattice strain.

Applying the above for the K–O bonds in our dioctahedral phengite- $2M_1$, which shows anisotropic interlayer region expansion (Mookherjee *et al.*, 2001), we find that the bonds with a negative coefficient of thermal expansion have a negative inner strain component, indicating the dominance of the inner deformation over the external deformation. It is this inner deformation, which renders the whole term negative (the only exception being the K–O6 bond). Although in this case the lattice deformation seems to dominate the inner deformation, it is still negative, maintaining the trend of the other short bonds (Table 3, data obtained for muscovite- $2M_1$ by Catti *et al.* (1989) are shown for comparison).

We also looked at the net displacement of the individual atoms within the asymmetric unit. The displacements (Δs) can be expressed in terms of the Cartesian coordinates as *X*, *Y*, *Z* with *X* || [100], *Y* ||

[010] and
$$Z \perp$$
 (001),
where $\Delta s = \sqrt{(\Delta X)^2 + (\Delta Y)^2 + (\Delta Z)^2}$,

and $\Delta X = a\Delta x + (c^*\cos\beta)\Delta z$; $\Delta Y = b\Delta y$; $\Delta Z = (c^*\sin\beta)\Delta z$. We find that the maximum displacement is shown by the basal O atoms. Their thermal induced relaxation is particularly confined to the *XY* plane, and probably controls all possible macroscopic distortions in and around the interlayer region (Table 4).

TABLE 4. Thermally-induced displacement of individual atoms, Δs .

	Δs (Å)	ΔX	ΔY
K (interlayer)	0.047		
Al,Fe,Mg (octahedral)	0.013		
T1 (tetrahedral)	0.035		
T2 (tetrahedral)	0.057		
O1 (apical)	0.018		
O2 (apical)	0.027		
O4 (basal)	0.115	0.112	0.025
O5 (basal)	0.145	0.134	0.055
O6 (basal)	0.099	-0.048	-0.086



FIG. 7. Temperature evolution of the MIR powder spectra representing Si-O stretching bands.

We attribute this substantial tetrahedral rotation, measured by α , and also the splitting of K–O stretching into K–O_{inner} and K–O_{outer}, to large inner-strain effects for the basal oxygen atoms. The value of α changes from ~8° (ECoN ~10) at 373 K to ~6° (ECoN ~11) at 973 K (Mookherjee *et al.*, 2001). Corresponding changes for muscovite-2 M_1 are 11° at 298 K to ~8° at 973 K (Catti *et al.*, 1989).

Behaviour of the tetrahedra

The Si-O-stretching vibrations observed by MIR absorption can be broadly classified into Si-Oapical (perpendicular) and Si-O_{basal} (in-plane) vibrations. The perpendicular vibration can be ascribed principally to a_1^1 with some contribution from a_1^2 (Farmer & Russell, 1964). Spectra in the IR region of $800-1200 \text{ cm}^{-1}$ for temperatures 300 to 460 K (with 20 K intervals) are shown in Fig. 7. The peak at ~1080 cm⁻¹ is attributed to Si-O_{apical} stretching (Serratosa, 1960; Farmer & Russell, 1964; Velde, 1978). Two strong absorption bands, at $\sim 1000 \text{ cm}^{-1}$ and 1020 cm⁻¹ are assigned to Si-O_{basal} stretching (Farmer & Russell, 1964). The peak at \sim 910 cm⁻¹ may be assigned to Al-O(H)-Al bending (Farmer, 1974), whereas that at $\sim 830 \text{ cm}^{-1}$ is assigned to various Si-O-Al vibrations (Farmer & Russell, 1964; Farmer, 1974). Within the temperature range of the IR experiments we observe only weak changes in the Si-O_{apical} stretching mode. On deconvoluting the spectra in Fig. 7 with four Lorentzian peaks, we obtain their thermal dependence as shown in Fig. 8. The peak assigned to Si-O_{apical} varies from ~1078 cm⁻¹ at 300 K to 1074 cm^{-1} at 460 K with only a 0.37% change in the stretching-mode frequency. The two peaks assigned to the Si-O_{basal} stretching vary from 1030 cm^{-1} at 300 K to 1025 cm⁻¹ at 460 K and 999 cm⁻¹ at 300 K to 992 cm⁻¹ at 460 K respectively, corresponding to changes of only 0.49 and 0.77% respectively. Though observed across different temperature ranges, these changes are very weak compared to the values obtained in the FIR region (2.4% change). The calculated mode



FIG. 8. Variation of Si-Ostretch modes [deconvoluted into Si-Oapical and Si-Obasal] bond length with temperature.

Grüneissen parameter ($\gamma_j = \partial \ln v_j \partial \ln V$; where v_j represents the Si–O_{apical} stretching frequency and *V* is the unit-cell volume) for the Si–O_{apical} stretching mode is ~0.65 indicating the contribution of the mode towards the total volume changes (considering the same temperature range for both frequency and volume changes). This value is comparable to 0.65 for the Si(Al)–O stretching modes (1040 cm⁻¹) in albite (Zhang *et al.*, 1996).

From the neutron diffraction study of Mookherjee *et al.* (2001) we find substantial movement of the tetrahedral atoms away from the basal plane of oxygen. The relationship between τ and T_{disp} for the two crystallographically distinct tetrahedral sites T(1) and T(2) is shown in Fig. 9. Note that there is considerable deviation from the ideal tetrahedral $\langle \overline{O}_{\text{apical}} - T - O_{\text{basal}} \rangle$ angle of 109°28' for an undistorted tetrahedron. There is a positive correlation between the tetrahedral flattening angle and

 $T_{\rm disp}$, which varies from 0.0716 Å at 373 K to 0.1526 Å at 973 K. On the timescale of our experiments, the mean $O_{\rm apical}-T-O_{\rm basal}$ angle increases for both the T(1) and the T(2) sites indicating thickening of the tetrahedral sheet. The $\langle \overline{T(1)} - O(6) - T(2) \rangle$, $\langle \overline{T(1)} - O(5) - T(2) \rangle$ and $\langle \overline{T(1)} - O(4) - T(2) \rangle$ angle varies from 127.42° (373 K) to 123.93° (973 K); 141.75° (373 K) to 140.90° (973 K) and 132.16° (373 K) to 128.39° (973 K) respectively. The decrease of these $\langle \overline{T(1)} - O_{\rm basal} - T(2) \rangle$ bond angles is probably related to differential movement of the T(1) and T(2) cations towards the apical O(1) and O(2) ions respectively.

CONCLUSIONS

On the basis of results from *in situ* high-temperature neutron powder diffraction and FTIR



FIG. 9. Correlation between $T_{\text{disp}}(\text{\AA})$ and $\tau(^{\circ})$ for the two distinct crystallographic sites T(1) and T(2) as shown in Fig. 1.

spectroscopic experiments in FIR (300-610 K) and MIR (300-460 K) regions, we can identify the nature of the anisotropic expansion of the interlayer region of phengite. The ditrigonal distortion decreases (8° at 373 K to $\sim 6^{\circ}$ at 973 K) with temperature, because the shorter contacts expand and the longer bonds contract. The frequency of the corresponding K-Oinner stretch decreases with temperature, confirming the increase in length of the short bonds as observed by neutron data. The large-scale strain in the unit cell can be expressed as a combined effect of lattice deformation (expansion) and inner deformation. The tetrahedral flattening angle and T_{disp} are correlated, indicating the apparent movement of the tetrahedral cation away from the basal plane.

We attribute all these changes to the combined effect of individual microsopic atomic displacements (inner strains) of the basal oxygen atoms, which cause the tetrahedra to rotate, and induce anisotropic expansion of the interlayer cavity. Finally, these displacements are responsible for differential movement of the two tetrahedral cations.

ACKNOWLEDGMENTS

The authors thank Ming Zhang for assistance with the FTIR experiments. The authors are also grateful to Stephen Guggenheim and Bruce Velde for their helpful reviews. MM acknowledges the financial support of the Cambridge Commonwealth Trust and the ORS.

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Appendix

METRIC MATRIX AND ITS APPLICATION

Origin of metric matrix

Let us consider [a, b, c] as our coordinate system. Then the scalar/dot product between two vectors

$$\mathbf{r}_1 = x_1 \mathbf{a} + y_1 \mathbf{b} + z_1 \mathbf{c}$$
 and $\mathbf{r}_2 = x_2 \mathbf{a} + y_2 \mathbf{b} + z_2 \mathbf{c}$;

is

$$\mathbf{r}_{1} \cdot \mathbf{r}_{2} = (x_{1}\boldsymbol{a} + y_{1}\boldsymbol{b} + z_{1}\boldsymbol{c}).(x_{2}\boldsymbol{a} + y_{2}\boldsymbol{b} + z_{2}\boldsymbol{c})$$

= $x_{1}x_{2}a^{2} + y_{1}y_{2}b^{2} + z_{1}z_{2}c^{2} + (x_{1}y_{2} + x_{2}y_{1}) ab \cos\gamma + (x_{1}z_{2} + x_{2}z_{1}) ac \cos\beta + (y_{1}z_{2} + z_{2}y_{1}) bc \cos\alpha$

or, in matrix notation

$$\mathbf{r}_{1} \cdot \mathbf{r}_{2} = \begin{pmatrix} x_{1} & y_{1} & z_{1} \end{pmatrix} \begin{pmatrix} a \times a & a \times b \times \cos \gamma & a \times c \times \cos \beta \\ b \times a \times \cos \gamma & b \times b & b \times c \times \cos \alpha \\ c \times a \times \cos \beta & c \times b \times \cos \alpha & c \times c \end{pmatrix} \begin{pmatrix} x_{2} \\ y_{2} \\ z_{2} \end{pmatrix} = X^{\mathrm{T}} G X$$

where

$$G = \begin{pmatrix} a \times a & a \times b \times \cos \gamma & a \times c \times \cos \beta \\ b \times a \times \cos \gamma & b \times b & b \times c \times \cos \alpha \\ c \times a \times \cos \beta & c \times b \times \cos \alpha & c \times c \end{pmatrix}$$

is defined as the metric matrix. Its elements define both the moduli of a, b, and c and the angles between them. The value of its determinant is equivalent to the square of the unit-cell volume and is given as

$$\mathbf{G} = a^2 b^2 c^2 (1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + \cos \alpha \cos \beta \cos \gamma) \approx \text{Volume}^2 = (\mathbf{a} \cdot \mathbf{b} \times \mathbf{c})^2$$

Now let us consider a special case when $\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}$. Then the scalar product equation becomes $\mathbf{r}^2 = X^T G X = x^2 a^2 + y^2 b^2 + z^2 c^2 + 2xy \ ab \ \cos\gamma + 2xz \ ac \ \cos\beta + 2yz \ bc \ \cos\alpha$ which gives the modulus squared of the vector. We can use this relation to calculate the inter-atomic distances between two atoms with fractional coordinates (x_1, y_1, z_1) and (x_2, y_2, z_2) . We denote $\Delta_1 = a(x_1 - x_2)$; $\Delta_2 = b(y_1 - y_2)$ and $\Delta_3 = c(z_1 - z_2)$, which gives $d^2 = \Delta_1^2 + \Delta_2^2 + \Delta_3^2 + 2\Delta_1 \Delta_2 \cos\gamma + 2\Delta_1 \Delta_3 \cos\beta + 2\Delta_2 \Delta_3 \cos\alpha$.