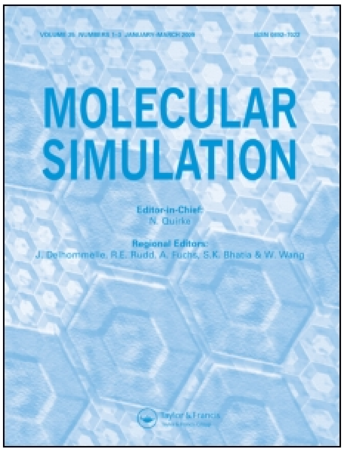

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Interatomic Potentials for Micas

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Preliminary Communication

INTERATOMIC POTENTIALS FOR MICAS

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We investigate the transferability of short range interatomic potentials and the applicability of the fully ionic model to the simulation of the layer structured mica, muscovite, using energy minimisation and free energy minimisation techniques.

KEY WORDS: Interatomic potential, energy minimisation, free energy minimisation, mica, muscovite

INTRODUCTION

Micas are an important group of rock forming minerals which possess a layered structure. Although their structures are reasonably well known, their crystal properties have generally not been determined. Hence it is impractical to fit an empirical potential model to micas, and therefore necessary to transfer potential parameters derived by fitting to binary compounds, or calculated by theoretical methods.

In this communication we address the following questions:

Is the fully ionic model, with 3 body bond-bending terms, applicable to the simulation of micas?

Is the transferability of short range potentials a useful approximation for modelling micas?

We attempt to answer these questions by modelling the mica, *muscovite*, and comparing its simulated properties with those measured experimentally. These properties include the only complete set of elastic constants reported for a mica [1].

STRUCTURE

The structure of a muscovite is shown in Figure 1. The aluminosilicate layers are negatively charged and comprise two types of sheet;

(i) 2 corner sharing tetrahedral sheets (constructed from Al/SiO_4 tetrahedra)
(ii) 1 edge sharing octahedral sheet (comprising AlO_6 octahedra)

The layers are held together by charge balancing interlayer cations.

The *intralayer* bonding is much stronger than the *interlayer* bonding. Consequently the crystal structure is far more rigid within the layers than between the layers, which is reflected in its elastic properties, discussed below.

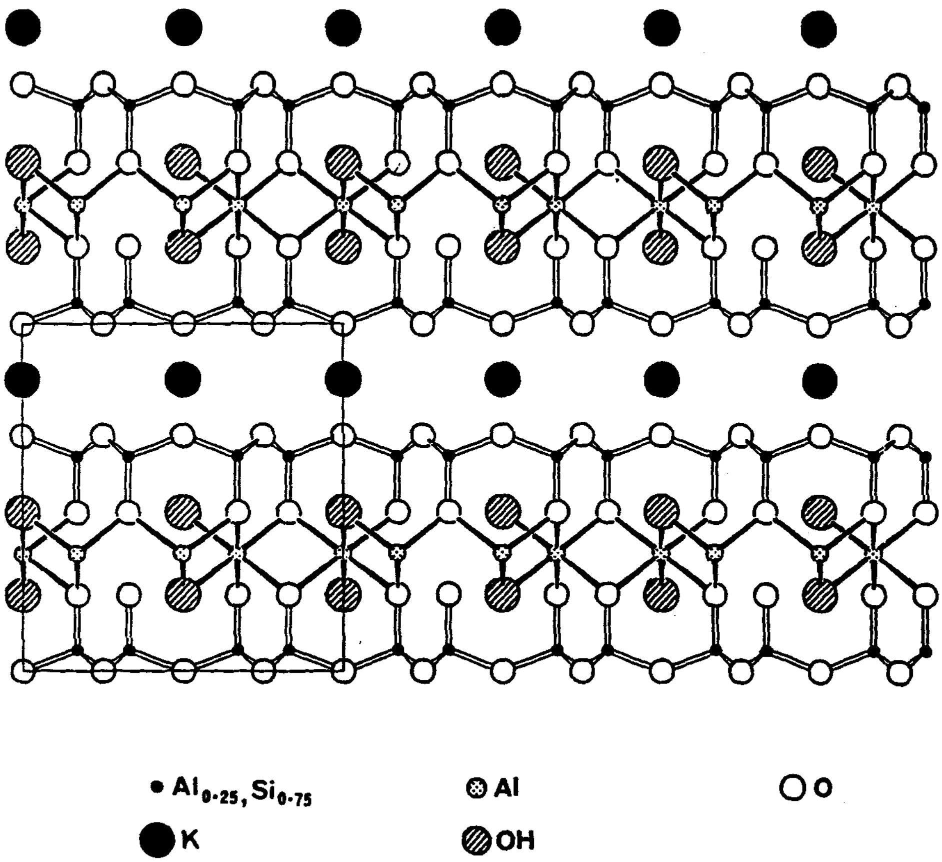

Figure 1 The structure of Muscovite.

CHEMISTRY

The chemistry of micas is complex and diverse. However, in order to simplify our model, we limit our discussion to the end member composition of muscovite.

$$K \quad Al_2 \quad Al,Si_3 \quad O_{10} \quad (OH)_2$$

K -Interlayer cation
Al_2 -Octahedral cations
Al,Si_3 -Tetrahedral cations

TECHNIQUES

We have employed *energy minimisation* using the THBREL code [2] to simulate the structure at O K, and also *free energy minimisation* using the PARAPOCS code [3] to include the lattice dynamical effects of temperature in the simulation.

Table 1 Potential Parameters (All fitted to a Buckingham function except * which is fitted to a Morse function)

(i) Short Range Interaction	*A/eV*	ϱ/*Å*	*C/eV Å*$^{-6}$	*Ref.*
Si^{4+} – O^{2-}	1283.9073	0.3205	10.6616	[7]
Si^{4+} – $O^{1.426-}$(H)	999.98	0.3012	0.0	[8]
Al^{3+} – O^{2-}	1460.3	0.29912	0.0	[9]
K^{+} – O^{2-}	65269.710	0.2130	0.0	[10]
O^{2-} – O^{2-}	22764.0	0.149	27.88	[7,11]
	D_e/eV	β/Å^{-1}	r_e/Å	
*$H^{0.426+}$ – $O^{1.426-}$	7.0525	2.1986	0.9485	[12]
(ii) Shell Model Species				
	Y|e|	K/eVÅ^{-2}		
O^{2-}	−2.86902	74.92		[7]
(iii) Three body Interaction				
	K_B/eV rad^{-2}	θ_0		
O^{2-} – Si^{4+} – O^{2-}	2.09724	109.47		[7]

POTENTIAL MODEL

Several approximations to the potential model have been made because of the large number of different ion-ion interactions and uncertainties in the distribution of Al and Si cations within the tetrahedral sheets. We give a very brief account here; a more detailed discussion is given elsewhere [4].

All potentials have been fitted to a Buckingham function except the *intra*-molecular interaction of the hydroxide group which was fitted to a Morse function. The parameters for the short range interactions are given in Table 1.

The distribution of Si/Al in the tetrahedral sheets of $2M_1$ muscovite shows no long range ordering [5,6]. The explicit inclusion of tetrahedral Al and Si in the simulations would violate the accepted space group symmetry by incorrectly imposing long range ordering. In this study we report simulations that used a hybrid species of charge +3.75 to represent an average tetrahedral cation, although details of simulations including Al and Si explicitly in the tetrahedral sheets of micas can be found elsewhere [4].

At present it is not possible to derive *ab initio* 3 body potentials for tetrahedral O–Al–O and O–Si–O interactions. All the available potentials for these interactions have been fitted empirically, therefore the physical significance of individual parameters is uncertain, and any averaging of the parameters to obtain a short range potential for the hybrid species will be of doubtful value. Indeed our attempts to derive a reliable 3 body potential for the hybrid tetrahedral species from existing empirical 3 body O–Al–O and O–Si–O potentials has proved unsuccessful. For this reason we use an empirical 3 body O–Si–O potential [7] to represent the short range interactions of the hybrid species with oxygen. This includes bond bending terms about the O–Si–O bond angles.

The other short range cation — oxygen interations include an empirical 2 body Si–O potential [8] where the oxygen is part of the hydroxide group; an empirical Al–O potential [9] where aluminium is the octahedral cation; and an electron gas K–O

Table 2 Unit cell dimensions and bond lengths of muscovite. (All in angstroms and degrees)

CELL DIMENSION	*EXPT [13]*	*0 K Simulation*	*300 K Simulation*
a	5.204	5.246	5.254
b	9.018	9.179	9.195
c	20.073	19.783	20.009
β	95.82	96.53	96.53
mean $\mathrm{Al_{0.25}Si_{0.75}}-0$	1.644	1.620	1.622
mean Al-O, OH	1.934	1.932	1.934
O-H	0.920	0.975	0.975
mean $\mathrm{K-O_{outer}}$	3.353	3.331	3.354
mean $\mathrm{K-O_{inner}}$	2.872	2.980	3.020

potential [10] where potassium is the interlayer cation. The O–O potential was calculated *ab initio* [7], but includes a dispersion term fitted empirically [11]. The O–H potential [12] used to describe the *intra*-molecular interaction of the hydroxide group was calculated *ab initio*. Longer range hydrogen bonds (OH–O) are assumed to be purely electrostatic.

RESULTS AND DISCUSSION

(a) Structure

The unit cell dimensions and bond lengths are modelled well, within 2% of experimental data [13], (Table 2). We correctly model the thermal expansion to be greater between the layers than within the layers. However, due to the inherent difficulties of modelling the relatively weak interlayer bonding, we over-estimate the expansion between the layers.

Table 3 Experimental and calculated Elastic Moduli for Muscovite. Axes of elasticity system are defined as x parallel to **a**, and **z** parallel to **c**.

Elastic Stiffness Constants $10^{10} NM^{-2}$	*Expt [1]*	*OK simulation*	*300 K simulation*
C_{11}	18.43	22.87	22.85
C_{22}	17.84	23.27	23.32
C_{33}	5.91	6.56	5.72
C_{44}	1.60	1.63	1.03
C_{55}	1.76	1.73	1.28
C_{66}	7.24	7.62	7.65
C_{23}	2.17	2.24	1.62
C_{13}	2.38	2.50	1.98
C_{12}	4.83	9.84	9.51
C_{15}	−0.20	−0.19	−0.17
C_{25}	0.39	0.69	0.44
C_{35}	0.12	0.17	0.07
C_{46}	0.05	0.48	0.28

Table 4 Dielectric constants of muscovite. Axes of dielectric tensor are defined as **x** parallel to **a**, and **z** parallel to **c***.

(a) Static dielectric constant				
Expt.	*[14]*		*0 K Simulation*	*300 K Simulation*
	5.71	ε_{11}	5.62	5.84
		ε_{22}	5.30	5.50
		ε_{33}	5.47	5.53
(b) High frequency dielectric constant				
Expt.	*[1]*		*0 K Simulation*	*300 K Simulation*
	2.43-2.54*	ε_{11}	1.78	1.77
		ε_{22}	1.83	1.82
		ε_{33}	1.81	1.79

* from Refractive indices of muscovite at 488 nm.

(b) Elastic properties

The close agreement between our calculated values and experimental data [1] adds further confidence to our potential model, as is evident from Table 3. This includes the use of hybrid species to represent the tetrahedral cations. We reproduce the large acoustic anisotropy in the compressional moduli ($C_{11} \sim C_{22} > > C_{33}$), which arises from the weak interactions between the layers.

(c) Dielectric properties

Only the bulk static dielectric constant of muscovite has been measured [14]; this is in excellent agreement with our calculated values for the elements of the dielectric tensor, Table 4a. The high frequency dielectric constants are obtained from refractive indices [1], and are significantly higher than our calculated values, Table 4b. This discrepancy probably arises because a description of electronic polarisation is included only for anions (cations are treated as rigid ions).

CONCLUSIONS

The good agreement between calculated and experimental properties of muscovite indicates that:

Although exhibiting appreciable covalency, the fully ionic potential model with 3 body bond bending terms, is applicable to micas.

The transferability of short range potentials appears to be a useful approximation, enabling reliable predictions to made for other micas whose crystal properties have not been measured. The results illustrate the general transferability of the O–Si–O potential derived in reference [7].

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