

A New Approach to the Calculation of Electrostatic Energy Relations in Minerals: The Dioctahedral and Trioctahedral Phyllosilicates

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A NEW APPROACH TO THE CALCULATION OF ELECTROSTATIC ENERGY RELATIONS IN MINERALS: THE DIOCTAHEDRAL AND TRIOCTAHEDRAL PHYLLOSILICATES

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This paper presents an original and useful method for calculating and comparing the electrostatic component of the lattice energies of families of related, complex structures. The methodology and use of hypothetical, tractable steps in passing from one structure to another can be extended to families of crystal structures other than the phyllosilicates. Calculations made on a single ‘generic’ silicate, $\text{KX}_2\text{X}'\text{T}_4\text{O}_{10}(\text{OH})_2$, enables us to obtain the lattice energies of 1M aluminium mica, phlogopite, talc, pyrophyllite,

saponite, beidellite, illite, montmorillonite and hectorite and their fluorinated analogues. Site potentials are readily obtained when calculations are made in this manner. Considerable saving of computer time and effort coupled with little sacrifice of accuracy are a feature of this approach.

The paper further goes on to suggest how comparison of this type of generic calculation with the results obtained from calculations made on the true individual phyllosilicate structure can extend the potential information that can be gained from these studies.

The investigation of substitutional and relaxation energies of the phyllosilicates is considered. Surface energies (shown to be quadratic functions of x for micas derived from the structure $A_xX_2X'T_4O_{10}(OH)_2$, ($A = Na$ or K)) are calculated on the same principle, from, in this case, a 'generic' expanded lattice. The transferability principle introduced in this work enables us to make specific predictions regarding minerals for which single crystal X-ray diffraction studies are impractical. We attempt wherever possible an interpretation of the energies we calculate.

1. INTRODUCTION

Giese and coworkers (Giese 1971; Giese & Datta 1971; Giese *et al.* 1972; Giese 1973 *a, b*, 1974, 1975 *a, b*) have used simple electrostatic calculations to explain a variety of features concerning interlayer bonding in kaolinite, dickite, nacrite, diaspore, goethite, groutite, pyrophyllite, muscovite and various other minerals.

Born & Zemann (1964) and Sahl & Zemann (1965) have discussed structural features and distortions in garnets and zircon with the electrostatic approach. Ohashi & Burnham (1972) have investigated cation site distribution in pyroxene chains. Hougardy *et al.* (1976) have developed an electrostatic potential energy map for the vermiculite interlayer region.

Appelo (1977) has carried out calculations of the electrostatic energy of phlogopite, fluorphlogopite and annite. Such studies usually consist of a calculation on the individual minerals of interest (see Giese 1975 *a*), and by their very nature, require large amounts of computer time and are expensive to carry out.

The present paper proposes a method by which we can use a single calculation on a carefully chosen mineral to generate a wealth of information which can in turn produce reliable results for substitutionally and structurally related minerals, thus rendering separate calculations on them unnecessary.

The technique derives from the method developed by Jenkins and coworkers for the treatment of lattice energies of complex salts in that it parametrizes the electrostatic lattice potential energy as a function of charge (Jenkins & Waddington 1971, 1972; Jenkins & Pratt 1977). We demonstrate the approach with reference to some dioctahedral and trioctahedral micas and show that, from a single calculation, we can estimate electrostatic energies of silicates that can be derived by processes of substitution from the parent (generic) mineral chosen. We further show the same principles applied to individual structures and expanded structures can lead to considerations of hydroxyl orientation energies, surface energies, etc.

Two notes of caution should, however, be injected at this stage. First, while the electrostatic lattice energies predicted by this approach are, by any standards, very satisfactory, steps discussed that involve relaxation (symmetry changes or the orientation of OH ions), of necessity involve the calculation of quite small differences between very large total energies. This, in itself, suggests that we should be cautious in our interpretation of these relatively small differences. However, these differences are also influenced by repulsion and dispersion interactions (which are not the

subject of this paper) and may be rather sensitive to them. Thus, while for relaxation energies we appear to obtain consistent results, until further studies are made (and such are already in progress) we cannot be sure of the quantitative significance of these energy changes.

The second note of caution concerns the use of the ionic model and its applicability to structures possessing cations of high formal charge. The models used here and by other workers must be judged on the results that the calculations based on them ultimately generate. While the ionic approximation is undoubtedly a compromise, any attempt to institute 'covalent' corrections would, at this stage of the theory, be both untimely and unwise because of the total uncertainty that would surround such an approach.

What is clear, therefore, is that this paper seeks to establish the basic ideas of our new approach, offers suggestions as to how intercomparison of various results might be made, but reserves its view as to the significance of the differences in energy calculated until further calculations are completed.

2. SYMBOLS

$A_{ijklmnp}$	charge independent coefficient in electrostatic lattice potential energy equation
d_{hkl}	thickness of slice parallel to face (hkl)
E_i	interaction energy (per molecule or formula unit) between zeroth and i th layer
(hkl)	indices specifying crystal face
i, j, k, l, m, n, p	indices representing exponents of charges at various sites ($= 0, 1$ or 2)
(r, s)	coordinates of ionic chain parallel to direction $[uvw]$
O'	hydroxyl oxygen atom within the mica
$q_{Al}, q_K, q_F, q_H,$ $q_{Si}, q_O, q_{O'}$	charges on Al, K, F, H, Si, O and hydroxyl O' atoms
q_T	charge on atom T occupying tetrahedral site
q_X	charge on atom X occupying dioctahedral site (see X)
$q_{X'}$	charge on atom X' occupying trioctahedral site (see X')
T	tetrahedral site within the mica (usually corresponding to Si_3Al or Si_4 group)
$[uvw]$	specified direction in crystal
U_{att}	attachment energy when one slice of thickness d_{hkl} crystallizes on face (hkl)
U_{elec}	electrostatic lattice potential energy
U_{hyp}	electrostatic energy calculated by adiabatic substitution of charges while retaining site symmetry of generic structure
U_{relax}	relaxation energy ($= U_{true} - U_{hyp}$)
U_{subs}	'adiabatic' substitutional energy at a site or sites corresponding to retention of site position
U_{sl}	energy released when one slice of crystal is formed from its constituent ions
U_{surf}	surface energy of mica
U_{true}	electrostatic energy of structure calculated on basis of experimentally determined structural and positional parameters
U_i	interaction energy between ionic chains
U_{tet}	electrostatic relaxation energy (rotating or tilting, contraction or expansion) of tetrahedra in going from one structure to another
U_{OH}	electrostatic relaxation energy associated with movement of hydroxyl group position from one structure to another

$U_{\text{OH}}^{\alpha \rightarrow \perp}$	specific electrostatic relaxation energy change as OH goes from position α to the normal to perpendicular position
$U_{\text{m} \rightarrow \text{t}}$	monoclinic–triclinic transition energy
U_{oct}	specific electrostatic relaxation energy of octahedral positions in mica
V_j	site potential at ion j
$V_{j, \text{sl}}$	potential of ion j with respect to slice in which it lies
$V_{j, \text{att}}^{\pm}$	potential of ion j with respect to all slices (above) it (below)
V_{ρ}	unit cell volume
x	fraction of sites (Na or K) occupied by atoms compared to theoretical maximum ($0 \leq x \leq 1$)
X	site filled with Mg in trioctahedral mica and with Al in dioctahedral mica
X'	site filled with Mg in trioctahedral mica and empty in dioctahedral mica
y	defined for hectorite as fraction of Li atoms resident at X' site ($0 \leq y \leq 1$)
Z	number of molecules per period [uvw] in ionic chain

3. THEORY

The transformation of a trioctahedral mica $\text{KX}_2\text{X}'\text{T}_4\text{O}_{10}(\text{OH})_2$ into a dioctahedral mica $\text{KX}_2\text{T}_4\text{O}_{10}(\text{OH})_2$ can be considered to involve two stages. First, an X' atom is removed from the sites $(0, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, 0, \frac{1}{2})$, the process being carried out (a) so as to preserve electroneutrality:

$$q_{\text{X}'} + 2q_{\text{X}} = 6, \quad (1)$$

and (b) in such a way that all other atoms remain on their lattice sites. Secondly, the atoms in the resulting dioctahedral silicate rearrange their positions while achieving a total lattice energy minimum. Let us associate a substitutional energy, U_{subs} , with the first process and a relaxation energy, U_{relax} , with the second. A rearrangement of the tetrahedra and OH groups within the mica can accompany these changes. We shall express the total electrostatic lattice energy of the above structures in the general form

$$U_{\text{elec}} = \sum_{i=0}^2 \sum_{j=0}^{(2-i)} \sum_{k=0}^{(2-j)} \sum_{l=0}^{(2-k)} \sum_{m=0}^{(2-l)} \sum_{n=0}^{(2-m)} \sum_{p=0}^{(2-n)} A_{ijklmnp} q_{\text{K}}^i q_{\text{X}}^j q_{\text{X}'}^k q_{\text{T}}^l q_{\text{O}}^m q_{\text{O}'}^n q_{\text{H}}^p, \quad (2)$$

$i+j+k+l+m+n+p=2$

where the coefficients $A_{ijklmnp}$ are charge independent coefficients and q_{K} , q_{X} , $q_{\text{X}'}$, q_{T} , q_{O} , $q_{\text{O}'}$ and q_{H} are the charges on the potassium, dioctahedral X site, trioctahedral X' site (i.e. the extra site occupied by an atom in a trioctahedral mica when compared with a dioctahedral mica), T site (which may be Si_4 , Si_3Al , etc.), oxygen, hydroxyl oxygen (O') and hydrogen sites.

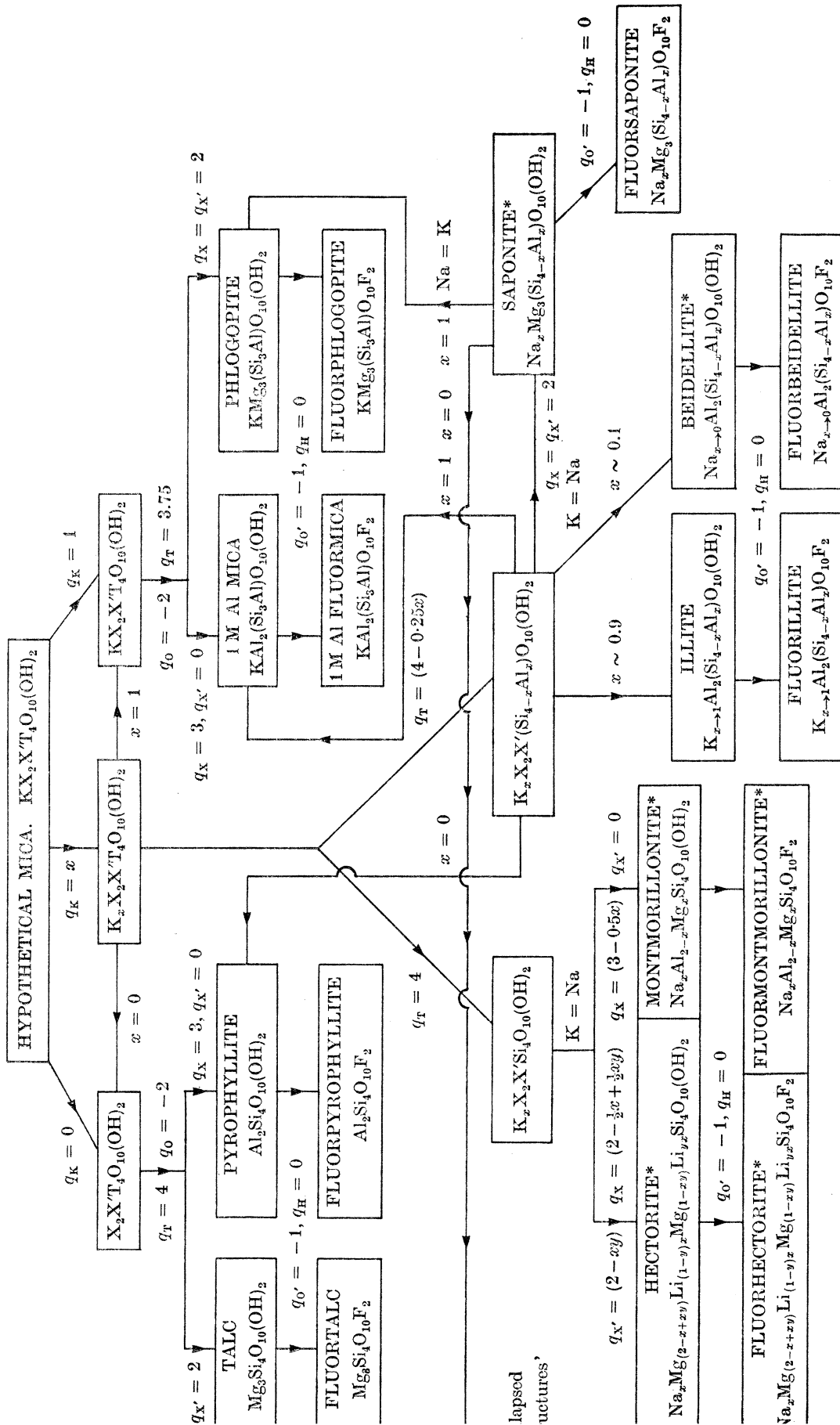
It will be clear that the transformation of an OH silicate into the corresponding F silicate (assuming no relaxation energy) is achieved by putting $q_{\text{O}'} = q_{\text{F}} = -1$ and $q_{\text{H}} = 0$ in the above expression. The energy of substitution of Al by Mg is obtained from the differences in U_{elec} calculated when $q_{\text{X}} = 3$, $q_{\text{X}'} = 0$ (dioctahedral silicate) and when $q_{\text{X}} = q_{\text{X}'} = 2$ (trioctahedral silicate). Taking a statistical average $\frac{1}{4}(3q_{\text{Si}} + q_{\text{Al}})$ corresponding to $q_{\text{T}} = 3.75$ for the arrangement where $\text{T} = \text{Si}_3\text{Al}$, we can obtain U_{subs} for a process where Si_3Al is replaced by Si_4 by considering $U_{\text{elec}}(q_{\text{T}} = 4) - U_{\text{elec}}(q_{\text{T}} = 3.75)$; the associated removal of K atoms corresponds to reducing q_{K} from 1.0 to zero. It should be noted moreover that, for example,

$$V_{\text{K}} = \left(\frac{\partial U_{\text{elec}}}{\partial q_{\text{K}}} \right)_{q_{\text{X}} q_{\text{X}'} q_{\text{T}} q_{\text{O}} q_{\text{O}'} q_{\text{H}}} = \sum_{i=0}^2 \sum_{j=0}^{(2-i)} \sum_{k=0}^{(2-j)} \sum_{l=0}^{(2-k)} \sum_{m=0}^{(2-l)} \sum_{n=0}^{(2-m)} \sum_{p=0}^{(2-n)} i A_{ijklmnp} q_{\text{K}}^{(i-1)} q_{\text{X}}^j q_{\text{X}'}^k q_{\text{T}}^l q_{\text{O}}^m q_{\text{O}'}^n q_{\text{H}}^p \quad (3)$$

$i+j+k+l+m+n+p=2$

TABLE 1. GENERIC SCHEME SHOWING HOW A GENERAL LATTICE ENERGY CALCULATION ON THE MINERAL $K_xX_2X'T_4O_{10}(OH)_2$ CAN BE USED, WHEN PARAMETRIZED IN THE FORM OF EQUATION (2), TO GENERATE RESULTS FOR A VARIETY OF RELATED SILICATES

GENERIC STRUCTURE



is the conventional site potential of the potassium atom, V_K , as customarily defined. It is our contention that the expression of the electrostatic energy of minerals in the form of equation (2) is particularly revealing as far as cation and anion substitutional (electrostatic) exchange energies are concerned, and that combination with calculations on the individual structures produced can lead to the quantification of the energy changes in the silicates.

Table 1 shows, assuming that there is no relaxation of atoms from the K, X, X', T, O, O' and H sites of the parent hypothetical mica $KX_2X'T_4O_{10}(O'H)_2$, how other related di- and tri-octahedral micas can be conceived as being derived from the parent as a result of specific assignment of the site charges.

The computations described in this paper evaluate the coefficients $A_{ijklmnp}$ for both hypothetical (i.e. derived by substitution without relaxation) and true (i.e. from crystal structure data) di- and tri-octahedral micas and from these computations conclusions are drawn as to the magnitudes of the electrostatic components of the substitutional, exchange, surface and reorientational energies.

4. CALCULATIONS

Hypothetical structures

Hypothetical mica structures $KX_2X'T_4O_{10}(OH)_2$ based on the generic structure, 1M aluminium mica $KAl_2T_4O_{10}(OH)_2$ whose coordinates are given in table 2, are studied. This structure is based on that reported (Sidorenko *et al.* 1975) to have space group C2. Since, in accordance with the observed symmetry of phlogopite (McCauley *et al.* 1973) we would expect a space group C2/m, and since the deviations of the reported 1M Al mica structure from C2/m are small, we have introduced a mirror plane. The hypothetical mica structure of table 2 is derived from the Sidorenko *et al.* (1975) structure by replacement of the four Al atoms by four atoms X in equivalent positions and addition of a further two atoms X' in positions $(0, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, 0, \frac{1}{2})$, and in the subsequent calculation by maintaining the charges of X and X', q_X and $q_{X'}$ such that condition (1) holds. Equation (2) gives the electrostatic energy of such a structure in an appropriate form for our development, and the values of $A_{ijklmnp}$ coefficients are given in column 4 of table 3. Energies calculated from these coefficients will be referred to as 'hypothetical' in the sense that true structures, although similar to those we shall derive by site substitution, have slightly different atomic positions. If we make the site substitutional changes indicated by the charge assignments in table 1, the equation (2) reduces in the individual cases to those given below. Following the substitutional scheme in table 1 and putting $q_K = 0$, $q_T = 4$, $q_X = q_{X'} = 2$, $q_O = -2$, equation (2) reduces to:

$$U_{elec}(\text{talc}, Mg_3Si_4O_{10}(OH)_2) = \sum_{j=0}^2 \sum_{k=0}^{(2-j)} \sum_{l=0}^{(2-k)} \sum_{m=0}^{(2-l)} \sum_{n=0}^{(2-m)} \sum_{p=0}^{(2-n)} (-1)^m 2^{2(l+j+k+m)} A_{0jklmnp} q_O^n q_H^p \quad (4)$$

$j+k+l+m+n+p=2$

The condition $q_K = 0$, $q_T = 4$, $q_X = 3$, $q_{X'} = 0$, $q_O = -2$ leads to

$$U_{elec}(\text{pyrophyllite}, Al_2Si_4O_{10}(OH)_2) = \sum_{j=0}^2 \sum_{k=0}^{(2-j)} \sum_{l=0}^{(2-k)} \sum_{m=0}^{(2-l)} \sum_{p=0}^{(2-m)} (-1)^m 3^j 2^{2(l+m)} A_{0j0lmnp} q_O^n q_H^p \quad (5)$$

$j+k+l+n+p=2$

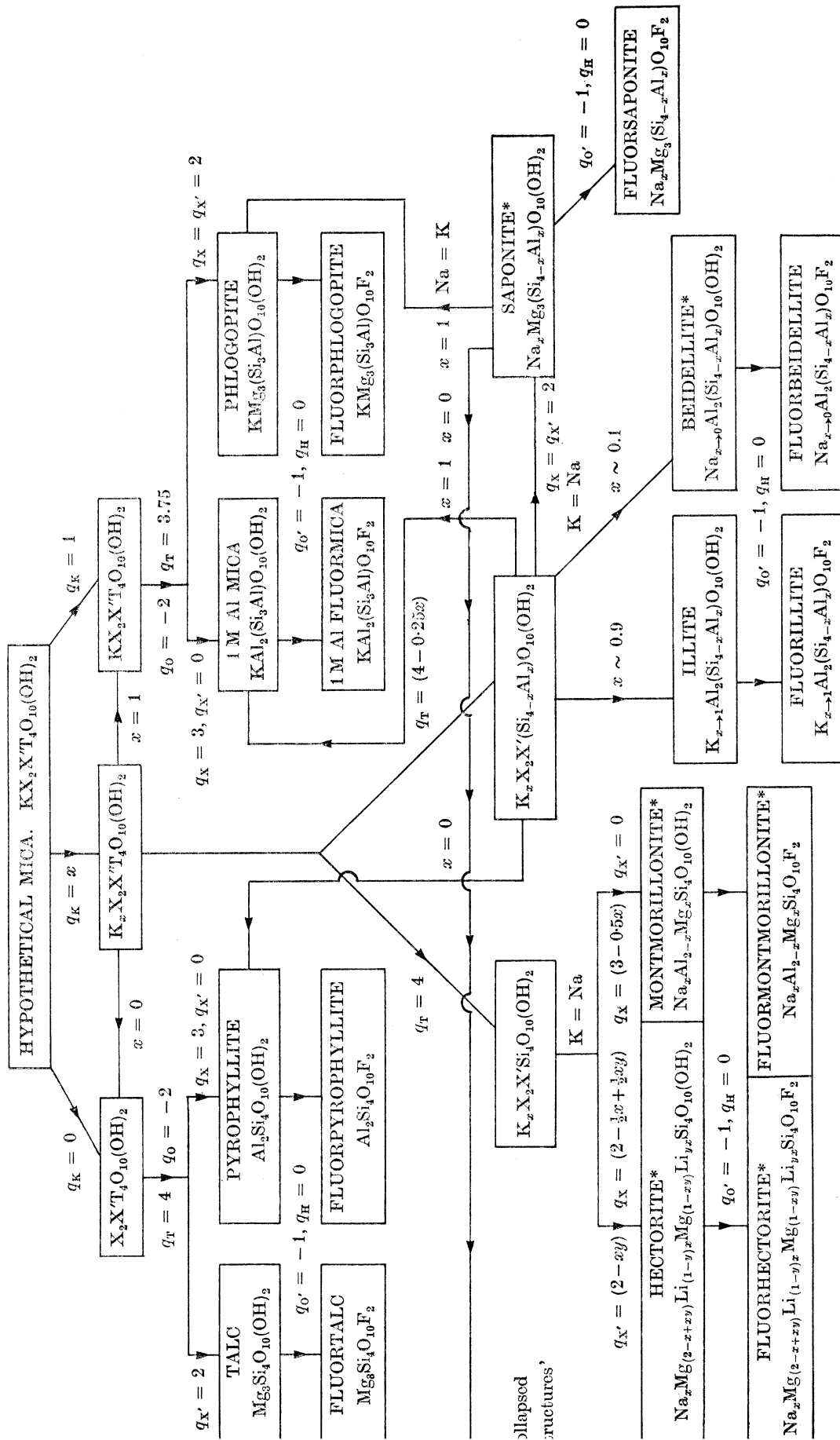
and condition $q_K = 1$, $q_T = 3.75$, $q_X = 3$, $q_{X'} = 0$, $q_O = -2$ leads to

$$U_{elec}(1M \text{ Al-mica}, KAl_2(Si_3Al)O_{10}(OH)_2) = \sum_{i=0}^2 \sum_{j=0}^{(2-i)} \sum_{l=0}^{(2-j)} \sum_{m=0}^{(2-l)} \sum_{n=0}^{(2-m)} \sum_{p=0}^{(2-n)} \times (-1)^m 3^{(j+l)} 2^{(n-2l)} 5^l A_{ij0lmnp} q_O^n q_H^p \quad (6)$$

$i+j+l+m+n+p=2$

TABLE 1. GENERIC SCHEME SHOWING HOW A GENERAL LATTICE ENERGY CALCULATION ON THE MINERAL $KX_2X'T_4O_{10}(OH)_2$ CAN BE USED, WHEN PARAMETRIZED IN THE FORM OF EQUATION (2), TO GENERATE RESULTS FOR A VARIETY OF RELATED SILICATES

GENERIC STRUCTURE



this equation reduces to equation (7) for phlogopite when $x = 1$ ($\text{Na} = \text{K}$) and to equation (4) for talc when $x = 0$.

Under the substitution $q_{\text{K}} = x$, $q_{\text{T}} = 4$, $q_{\text{X}} = (2 - 0.5x + 0.5xy)$, $q_{\text{X}'} = (2 - xy)$, $q_{\text{O}} = -2$ with $\text{K} = \text{Na}$, equation (2) generates the electrostatic energy for 'collapsed' hectorite having Li atoms at both X and X' sites:

$$U_{\text{elec}}(\text{'collapsed' hectorite, Na}_x\text{Mg}_{(2-x+xy)}\text{Li}_{(1-y)x}\text{Mg}_{(1-xy)}\text{Li}_{xy}\text{Si}_4\text{O}_{10}(\text{OH})_2) \\ = \sum_{i=0}^2 \sum_{j=0}^{(2-i)} \sum_{k=0}^{(2-j)} \sum_{l=0}^{(2-k)} \sum_{m=0}^{(2-l)} \sum_{n=0}^{(2-m)} \sum_{p=0}^{(2-n)} (-1)^m 2^{(m+2l)} x^i (2 - 0.5x + 0.5xy)^j (2 - xy)^k A_{ijklmnp} q_{\text{O}}^p q_{\text{H}}^p, \quad (12)$$

The substitution of $y = 1$ into equation (12) generates the situation where 'collapsed' hectorite

TABLE 3. $A_{ijklmnp}/(\text{kJ mol}^{-1})$ AS OBTAINED BY DIRECT CALCULATION FROM THE ATOMIC POSITIONS GIVEN IN TABLE 2

$ijklmnp$	interaction involved	$A_{ijklmnp}/(\text{kJ mol}^{-1})$			
		1M Al mica (table 2) $C = 10.12 \text{ \AA}$	hypothetical 1M mica (table 2) $C = 10.12 \text{ \AA}$	expanded hypothetical 1M mica (table 8) $C = 15.32 \text{ \AA}$	expanded hypothetical 1M mica (table 8) $C = 20.24 \text{ \AA}$
2000000	KK	254.4	254.4	513.3	508.8
1100000	KX	619.2	619.2	1227.8	619.2
1010000	KX'	0	309.0	613.3	309.0
1001000	KT	276.2	276.2	1146.3	275.6
1000100	KO	795.8	795.8	3008.3	795.4
1000010	KO'	524.2	524.2	1106.6	524.2
1000001	KH	486.5	486.5	1057.2	486.5
0200000	XX	300.8	300.8	-336.4	-939.7
0110000	XX'	0	-416.0	-1053.3	-1656.6
0101000	XT	884.5	884.4	-930.9	-2995.1
0100100	XO	319.8	319.8	-4297.2	-9500.9
0100010	XO'	-1008.2	-1008.2	-2227.8	-3407.6
0100001	XH	-515.8	-515.8	-1710.3	-2879.0
0020000	X'X'	0	254.4	95.1	-55.7
0011000	X'T	0	455.9	-451.9	-1484.0
0010100	X'O	0	423.4	-1885.4	-4487.2
0010010	X'O'	0	-421.0	-1030.7	-1620.7
0010001	X'H	0	-772.3	-1369.6	-1954.0
0002000	TT	1814.1	1814.1	734.8	-983.1
0001100	TO	-980.8	-980.8	-6538.0	-15204.1
0001010	TO'	833.9	833.9	-870.9	-2882.9
0001001	TH	716.7	716.7	-939.3	-2928.1
0000200	OO	6290.2	6290.2	-854.9	-11787.4
0000110	OO'	1228.5	1228.5	-3112.7	-8184.5
0000101	OH	1091.0	1091.0	-3127.8	-8141.9
0000020	O'O'	486.3	486.3	-95.6	-672.4
0000011	O'H	-1695.5	-1695.5	-2834.1	-3976.9
0000002	HH	592.7	592.7	35.4	-530.0

has Li atoms solely at the X' sites (i.e. corresponding to the empty octahedral positions of our 1M Al mica). The corresponding electrostatic energy is given by

$$U_{\text{elec}}(\text{'collapsed' hectorite, Na}_x\text{Mg}_{(3-x)}\text{Li}_x\text{Si}_4\text{O}_{10}(\text{OH})_2) \\ = \sum_{i=0}^2 \sum_{j=0}^{(2-i)} \sum_{k=0}^{(2-j)} \sum_{l=0}^{(2-k)} \sum_{m=0}^{(2-l)} \sum_{n=0}^{(2-m)} \sum_{p=0}^{(2-n)} (-1)^m 2^{(j+m+2l)} x^i (2-x)^k A_{ijklmnp} q_{\text{O}}^n q_{\text{H}}^p, \quad (13)$$

and the corresponding substitution of $y = 0$ into equation (12) generates the situation where 'collapsed' hectorite has Li atoms solely at the X sites (i.e. corresponding to the Al positions in our 1M Al mica), in this case the electrostatic energy is given by:

$$U_{\text{elec}}(\text{'collapsed' hectorite, Na}_x\text{Li}_x\text{Mg}_{(3-x)}\text{Si}_4\text{O}_{10}(\text{OH})_2) \\ = \sum_{i=0}^2 \sum_{j=0}^{(2-i)} \sum_{k=0}^{(2-j)} \sum_{l=0}^{(2-k)} \sum_{m=0}^{(2-l)} \sum_{n=0}^{(2-m)} \sum_{p=0}^{(2-n)} (-1)^m 2^{(m+2l+k)} x^i (2-0.5x)^j A_{ijklmnp} q_{\text{O}}^n q_{\text{H}}^p, \quad (14)$$

If $q_{\text{K}} = x$, $q_{\text{T}} = 4$, $q_{\text{X}} = (3 - 0.5x)$, $q_{\text{X}'} = 0$, $q_{\text{O}} = -2$ and $\text{K} = \text{Na}$, equation (2) generates the electrostatic energy for 'collapsed' montmorillonite:

$$U_{\text{elec}}(\text{'collapsed' montmorillonite, Na}_x\text{Al}_{(2-x)}\text{Mg}_x\text{Si}_4\text{O}_{10}(\text{OH})_2) \\ = \sum_{i=0}^2 \sum_{j=0}^{(2-i)} \sum_{l=0}^{(2-j)} \sum_{m=0}^{(2-l)} \sum_{n=0}^{(2-m)} \sum_{p=0}^{(2-n)} (-1)^m 2^{(m+2l)} x^i (3-0.5x)^j A_{ij0lmnp} q_{\text{O}}^n q_{\text{H}}^p, \quad (15)$$

which reduces, when $x = 0$, to equation (5) for pyrophyllite.

The advantage which the above equations give when parametrized, over previous individual mineral calculations, is that from the coefficients in column 4 of table 3 we are able to generate all the electrostatic energies for the non-expanded structures in table 4, with the resulting 12-fold saving in computer time. Evaluation of the electrostatic energies as given in equations (4)–(15) gives the electrostatic lattice potential energies of 'adiabatic' structures obtained by removing atoms from the parent $\text{KX}_2\text{X}'\text{T}_4\text{O}_{10}(\text{OH})_2$ silicate, without the usual accompanying change in atomic coordinates.

In addition to these 'derived' electrostatic energies generated by the scheme in table 1, we can carry out calculations for true structures for which X-ray data are available.

True structures

Table 5 gives details of the sources of crystal structure data used to obtain electrostatic (charge independent) energy equations for true mica structures.

In the case of talc, the hydrogen coordinates, based on the structure of Raynor & Brown (1973), were taken to be (0.2276, 0.1677, 0.2198) and, in the case of pyrophyllite, the hydrogen coordinates, based on the structure of Wardle & Brindley (1972) were taken to be (0.148, 0.104, 0.159), in accordance with the work of Giese. In the case of phlogopite the O' (hydroxyl oxygen) positions were taken from the work of McCauley *et al.* (1973) on fluorphlogopite, the hydroxyl oxygen atoms being placed at the fluorine atom positions. The additional hydrogen positions were assumed to be (0.0992, 0.0000, 0.3015).

In the above talc and phlogopite structures, the O—H dipole is perpendicular to the mica layer

TABLE 4. ELECTROSTATIC ENERGIES CALCULATED BY 'ADIABATIC' SUBSTITUTION OF ATOMIC CHARGES IN EQUATION (2) WITH COEFFICIENTS FROM TABLE 3

q_K	substitution made						equation derived from (2) used in calculation	$A_{ijklmnop}$ from table 3, column 1	$U_{elec}/$ (kJ mol ⁻¹)	notes
	q_X	$q_{X'}$	q_T	q_O	$q_{O'}$	q_H				
0	2	2	4	-2	-2	1	(4)	2	78336.3	talc
0	2	2	4	-2	-2	1	(4)	3	78341.0	expanded talc
0	2	2	4	-2	-2	1	(4)	4	78343.2	expanded talc
0	2	2	4	-2	-1	0	(4)	2	72805.3	fluortalc
0	2	2	4	-2	-1	0	(4)	3	72810.4	exp. fluortalc
0	2	2	4	-2	-1	0	(4)	4	72812.0	exp. fluortalc
0	3	0	4	-2	-2	1	(5)	2	82792.3	pyrophyllite
0	3	0	4	-2	-2	1	(5)	3	82797.9	exp. pyrophyllite
0	3	0	4	-2	-2	1	(5)	4	82799.9	exp. pyrophyllite
0	3	0	4	-2	-1	0	(5)	2	76066.3	fluorpyrophyllite
0	3	0	4	-2	-1	0	(5)	3	76072.0	expanded fluorpyrophyllite
0	3	0	4	-2	-1	0	(5)	4	76073.5	expanded fluorpyrophyllite
1	3	0	3.75	-2	-2	1	(6)	2	79355.2	1M Al mica
$\frac{1}{2}$	3	0	3.75	-2	-2	1	(6)	3	79135.8	exp. 1M Al mica
$\frac{1}{2}$	3	0	3.75	-2	-2	1	(6)	4	79135.9	exp. 1M Al mica
1	3	0	3.75	-2	-1	0	(6)	2	72638.2	1M Al-fluormica
$\frac{1}{2}$	3	0	3.75	-2	-1	0	(6)	3	72417.5	exp. 1M Al fluormica
$\frac{1}{2}$	3	0	3.75	-2	-1	0	(6)	4	72417.1	exp. 1M Al fluormica
1	2	2	3.75	-2	-2	1	(7)	2	74891.8	phlogopite
$\frac{1}{2}$	2	2	3.75	-2	-2	1	(7)	3	74671.5	exp. phlogopite
$\frac{1}{2}$	2	2	3.75	-2	-2	1	(7)	4	74671.8	exp. phlogopite
1	2	2	3.75	-2	-1	0	(7)	2	69369.2	fluorphlogopite
$\frac{1}{2}$	2	2	3.75	-2	-1	0	(7)	3	69148.5	expanded fluorphlogopite
$\frac{1}{2}$	2	2	3.75	-2	-1	0	(7)	4	69148.2	expanded fluorphlogopite
0.1	3	0	3.975	-2	-2	1	(9)	2	82421.8	'collapsed' beidellite
0.05	3	0	3.975	-2	-2	1	(9)	3	82428.9	beidellite
0.05	3	0	3.975	-2	-2	1	(9)	4	82430.7	beidellite
0.1	3	0	3.975	-2	-1	0	(9)	2	75696.6	'collapsed' fluorbeidellite
0.05	3	0	3.975	-2	-1	0	(9)	3	75703.8	fluorbeidellite
0.05	3	0	3.975	-2	-1	0	(9)	4	75705.0	fluorbeidellite
0.9	3	0	3.775	-2	-2	1	(10)	2	79672.6	illite
0.45	3	0	3.775	-2	-2	1	(10)	3	79499.2	exp. illite
0.45	3	0	3.775	-2	-2	1	(10)	4	79499.5	exp. illite
0.9	3	0	3.775	-2	-1	0	(10)	2	72954.1	fluorillite
0.45	3	0	3.775	-2	-1	0	(10)	3	72780.2	exp. fluorillite
0.45	3	0	3.775	-2	-1	0	(10)	4	72779.9	exp. fluorillite

and the O—H distance has been taken as 1.000 Å.† In pyrophyllite the O—H distance is taken to be 0.969 Å and the O—H dipole makes an angle of 64° with the normal to the mica layer. In the 1M Al mica the O—H distance was again assumed to be 1.000 Å, and the angle between the O—H dipole is inclined at 78° to the normal of the mica layer.

The calculations for the true structures of table 5 lead to equations of the general form of (2) with the specific coefficients listed in table 6 for talc, pyrophyllite and 1M Al mica.

† 1 Å = 10⁻¹ nm = 10⁻¹⁰ m.

TABLE 5. TRUE MICA STRUCTURES USED IN CALCULATIONS

mineral	formula	structure	A/Å	B/Å	C/Å	cos α	cos β	cos γ	notes	source
talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	triclinic	5.293	9.179	9.496	-0.0099	-0.1549	-0.0005	H position as stated (see text)	Raynor & Brown (1973)
fluortalc	Mg ₃ Si ₄ O ₁₀ F ₂	triclinic	5.293	9.179	9.496	-0.0099	-0.1549	-0.0005	assuming O' position of talc occupied by F	Raynor & Brown (1973)
pyrophyllite	Al ₂ Si ₄ O ₁₀ (OH) ₂	triclinic	5.161	8.957	9.351	-0.0180	-0.1800	0.0044	H position as stated (see text)	Wardle & Brindley (1972)
fluorpyrophyllite	Al ₂ Si ₄ O ₁₀ F ₂	triclinic	5.161	8.957	9.351	-0.0180	-0.1800	0.0044	Assuming O' position of pyrophyllite occupied by F	Wardle & Brindley (1972)
1M Al mica	KAl ₂ T ₄ O ₁₀ (OH) ₂	monoclinic	5.186	8.952	10.120	0.0000	-0.2051	0.0000	space group adjusted to C2/m (see text)	Sidorenko <i>et al.</i> (1975)
1M Al fluor mica	KAl ₂ T ₄ O ₁₀ F ₂	monoclinic	5.186	8.952	10.120	0.0000	-0.2051	0.0000	Assuming O' position in 1M Al mica occupied by F	Sidorenko <i>et al.</i> (1975)
phlogopite	KMg ₃ T ₄ O ₁₀ (OH) ₂	monoclinic	5.308	9.183	10.139	0.0000	-0.1749	0.0000	Assuming position in fluorphlogopite occupied by O'.	McCauley <i>et al.</i> (1973)
fluorphlogopite	KMg ₃ T ₄ O ₁₀ F ₂	monoclinic	5.308	9.183	10.139	0.0000	-0.1749	0.0000	H position as stated (see text)	McCauley <i>et al.</i> (1973)

TABLE 6. $A_{ijklmnp}$ (kJ mol⁻¹) COEFFICIENTS AS OBTAINED FROM INDIVIDUAL CALCULATIONS ON TRUE STRUCTURES CONTAINING OH GROUP

(Equations for associated fluorine analogues are obtained by: halving the coefficients $A_{1000010}$, $A_{0100010}$, $A_{0010010}$, $A_{0001010}$ and $A_{0000110}$; quartering the coefficient $A_{0000020}$ and by setting to zero the coefficients $A_{1000001}$, $A_{0100001}$, $A_{0010001}$, $A_{0001001}$, $A_{0000101}$, $A_{0000011}$ and $A_{0000002}$.)

<i>ijklmnp</i>	interaction involved	values of $A_{ijklmnp}$ / (kJ mol ⁻¹)		
		talc $X_2X'Si_4O_{10}(OH)_2$ (X = X' = Mg, T = Si)	pyrophyllite $X_2Si_4O_{10}(OH)_2$ (X = Al, T = Si)	1M Al mica $KX_2(Si_3Al)O_{10}(OH)_2$ (X = Al, T = Si ₃ Al)
2000000	KK	0.0	0.0	254.4
1100000	KX	0.0	0.0	619.2
1010000	KX'	0.0	0.0	0.0
1001000	KT	0.0	0.0	276.2
1000100	KO	0.0	0.0	795.8
1000010	KO'	0.0	0.0	524.2
1000001	KH	0.0	0.0	486.5
0200000	XX	384.1	387.8	300.8
0110000	XX'	-316.6	0.0	0.0
0101000	XT	1072.5	1070.0	884.5
0100100	XO	985.0	764.6	319.8
0100010	XO'	-772.1	-872.3	-1008.2
0100001	XH	74.8	-241.3	-515.8
0020000	X'X'	271.2	0.0	0.0
0011000	X'T	536.0	0.0	0.0
0010100	X'O	479.2	0.0	0.0
0010010	X'O'	-386.1	0.0	0.0
0010001	X'H	35.9	0.0	0.0
0002000	TT	1793.9	1844.2	1814.1
0001100	TO	-1062.5	-796.4	-980.8
0001010	TO'	990.6	991.4	833.9
0001001	TH	607.2	779.6	716.7
0000200	OO	6355.5	6592.5	6290.2
0000110	OO'	1589.5	1572.0	1228.5
0000101	OH	1402.3	1361.8	1091.0
0000020	O'O'	573.0	560.2	486.3
0000011	O'H	-1296.2	-1555.3	-1695.5
0000002	HH	809.9	732.3	592.7

Since phlogopite contains Mg atoms in both the X and X' sites, and since in our calculations† no distinction was made between Mg in X and Mg in X', the equation for phlogopite was not evaluated strictly in accordance with equation (2), in that, for example, the coefficients $A_{1100000}$ and $A_{1010000}$, representing the K-X and K-X' interactions, were evaluated as a single coefficient representing the K-Mg interaction. The same is true for the X-X, X-X', X'-X' interactions (Mg-Mg); X-T, X'-T (Mg-T); X-O, X'-O (Mg-O) and X-H, X'-H (Mg-H) interactions. Since the results are not easily accommodated into the format of table 6 we present them separately for phlogopite:

† Parametrization of equation (16) could have been performed in such a way as to separate Mg(X) and Mg(X') contributions.

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$$\begin{aligned}
 U_{\text{elec}} (\text{phlogopite, true structure}) = & 253.3q_{\text{K}}^2 + 235.0q_{\text{K}}q_{\text{T}} + 891.1q_{\text{K}}q_{\text{Mg}} + 747.6q_{\text{K}}q_{\text{O}} \\
 & + 511.7q_{\text{K}}q_{\text{O}'} + 259.1q_{\text{K}}q_{\text{H}} + 1774.4q_{\text{T}}^2 + 1407.4q_{\text{T}}q_{\text{X}} \\
 & - 1037.1q_{\text{T}}q_{\text{O}} + 898.3q_{\text{T}}q_{\text{O}'} + 570.4q_{\text{T}}q_{\text{H}} + 180.7q_{\text{X}}^2 \\
 & + 908.9q_{\text{X}}q_{\text{O}} - 1436.1q_{\text{X}}q_{\text{O}'} - 138.3q_{\text{X}}q_{\text{H}} + 6202.8q_{\text{O}}^2 \\
 & + 1283.2q_{\text{O}}q_{\text{O}'} + 1240.9q_{\text{O}}q_{\text{H}} + 477.9q_{\text{O}'}^2 - 1436.4q_{\text{O}'}q_{\text{H}} \\
 & + 765.2q_{\text{H}}^2. \tag{16}
 \end{aligned}$$

The specific substitutions indicated in table 7 lead to the true electrostatic energies and to the derived (figures in parentheses) electrostatic energies for the minerals indicated, from the coefficients in table 6 (and for phlogopite, equation (16)).

TABLE 7. ELECTROSTATIC ENERGIES CALCULATED FROM TRUE STRUCTURES

(Values marked with an asterisk are calculated by adiabatic substitutions in equations of the form of equation (2) with the coefficients given in table 6, i.e. by assuming no relaxation energy.)

substitution made							generic structure	$U_{\text{elec}}/(\text{kJ mol}^{-1})$	mineral for which electrostatic energy is calculated
q_{K}	q_{X}	$q_{\text{X}'}$	q_{T}	q_{O}	$q_{\text{O}'}$	q_{H}			
0	2	2	4	-2	-2	1	talc	79599	talc
0	2	2	4	-2	-1	0	talc	73099	fluortalc
0	3	0	4	-2	-2	1	talc	(83673*)	(pyrophyllite)
0	3	0	4	-2	-1	0	talc	(75147*)	(fluorpyrophyllite)
0	3	0	4	-2	-2	1	pyrophyllite	83337	pyrophyllite
0	3	0	4	-2	-1	0	pyrophyllite	76348	fluorpyrophyllite
1	3	0	3.75	-2	-2	1	1M Al mica	79359	1M Al mica
1	3	0	3.75	-2	-1	0	1M Al mica	72641	1M Al fluormica
1	2	2	3.75	-2	-2	1	phlogopite	74915	phlogopite (OH)
1	2	2	3.75	-2	-1	0	phlogopite	68645	fluorphlogopite
0	2	2	4	-2	-2	1	phlogopite	(78608*)	(talc)
0	2	2	4	-2	-1	0	phlogopite	(72168*)	(fluortalc)

Expanded hypothetical structures

The first calculation of the electrostatic contribution to interlayer bonding was performed by Giese (1974) for the dioctahedral mica muscovite 2M_1 . His method is based on the comparison of the energies of a normal mica and of an expanded structure, the expansion of the structure being carried out in such a manner as to move the separate layers apart from each other until no further change in lattice energy was obtained on still further expansion of the layers. During this process, it is assumed that the layer itself remains intact, while the interlayer potassium ions were divided between the two separating layers in an ordered way. An interlayer separation of about 5 \AA appeared to be sufficient to make the remaining interlayer bonding almost negligible (i.e. no further change of electrostatic lattice energy occurred on expansion).

According to Giese, the difference between the lattice energies of the actual and the expanded structures gives the surface energy. This is an approximation, since if we write E_i as the interaction energy per molecule (or formula unit) between the zeroth and the i th layer, then Giese's method calculates $\sum_i E_i$. Since the actual surface or cleavage energy is the energy required to divide the *infinitely thick* crystal into two halves along the cleavage plane, it is given by the summation, $\sum_i iE_i$, which equals $\sum_i E_i$ only if higher terms can be neglected. This is indeed the case for mica where the layer is sufficiently thick, or for NaCl where, in the cleavage plane (001), all

ions lie in a plane. However, this is not always the case and other methods have been developed to deal with such cases (e.g. the Madelung method as discussed by Hartman (1973)). An ideal approach to the estimation of the surface energy would include a consideration of the role and contribution made by repulsion and dispersion energies.

Jenkins & Thakur (1979) are currently investigating the possibility of estimating these non-electrostatic contributions to the lattice energy of silicates, and some progress in this direction can already be reported.

In his subsequent work, Giese (1975*a, b*) has calculated the electrostatic energies of normal fluorine and hydroxyl silicates, and for the same structures separated by 9 Å. In this way, he obtains estimates of the interlayer bonding for both dioctahedral and trioctahedral micas. Pyrophyllite, muscovite $2M_1$, phlogopite and talc are all treated in this way.

In spite of the limitations alluded to above, the results generated by such studies are of inherent interest. Since it is the purpose of the present studies to contribute to this general theme, we have performed calculations for expanded mica structures derived from the hypothetical structure of table 2. In contrast to Giese, we divided the interlayer potassium ions between the two separated layers, giving each potassium ion a charge of $\frac{1}{2}q_K$. As a result, the space group symmetry changes from $C2/m$ to Cm although care has been taken to give a separate layer the symmetry $2/m$. The number of sites for which we have to calculate coefficients is doubled by this approach. Giese's alternative approach leads to an overall symmetry in the expanded structure corresponding to Pm , and, at the same time, quadruples the number of sites requiring consideration and would lead to a corresponding increase in the necessary computational effort. The results from Giese's study should reduce to those of the present study by superimposing a structure consisting of ions with a charge of $-\frac{1}{2}q_K$ on the potassium ions present in Giese's method and

TABLE 8. STRUCTURES USED FOR EXPANDED HYPOTHETICAL 1M MICAS DERIVED FROM Al MICA STRUCTURE (TABLE 2)

ion type	number in unit cell	charge on ion	15 Å expanded mica coordinates			20 Å expanded mica coordinates		
			<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
K	2	q_K	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
K	2	q_K	0.0000	0.0000	0.6606	0.0000	0.0000	0.5000
T	4	q_T	0.5803	0.1704	0.1524	0.5803	0.1704	0.1153
T	4	q_T	0.4197	0.1704	0.5082	0.4197	0.1704	0.3847
X	4	q_X	0.0000	0.1689	0.3303	0.0000	1.1689	0.2500
X'	2	$q_{X'}$	0.0000	0.5000	0.3303	0.0000	0.5000	0.2500
H	2	q_H	0.2739	0.0000	0.2472	0.2739	0.0000	0.1871
H	2	q_H	0.7261	0.0000	0.4134	0.7261	0.0000	0.3129
O	2	q_O	0.5159	0.0000	0.1215	0.5159	0.0000	0.0920
O	2	q_O	0.4841	0.0000	0.5391	0.4841	0.0000	0.4080
O	4	q_O	0.6520	0.1906	0.2592	0.6520	0.1906	0.1962
O	4	q_O	0.3480	0.1906	0.4014	0.3480	0.1906	0.3038
O	4	q_O	0.8283	0.2259	0.1093	0.8283	0.2259	0.0827
O	4	q_O	0.1717	0.2259	0.5513	0.1717	0.2259	0.4173
O'(H)	2	$q_{O'}$	0.0939	0.0000	0.2611	1.0939	0.0000	0.1976
O'(H)	2	$q_{O'}$	0.9061	0.0000	0.3995	1.9061	0.0000	0.3024
cell dimensions:			cell dimensions:			cell dimensions:		
$A = 5.186$			$A = 5.186$			$A = 5.186$		
$\cos \alpha = 0.0000$			$\cos \alpha = 0.0000$			$\cos \alpha = 0.0000$		
$B = 8.952$			$B = 8.952$			$B = 8.952$		
$\cos \beta = -0.2051$			$\cos \beta = -0.2051$			$\cos \beta = -0.2051$		
$C = 15.320$			$C = 15.320$			$C = 20.240$		
$\cos \gamma = 0.0000$			$\cos \gamma = 0.0000$			$\cos \gamma = 0.0000$		

ions with a charge $+\frac{1}{2}q_K$ on the sites not containing K^+ ions in the ordered arrangement assumed by Giese.

The coordinates of the expanded structures are obtained by separating the layers along the direction of the c axis. This means that in expanding structures only the unit cell dimension c changes, and for the atomic coordinates only z changes. The transformation changes the z coordinates into zc_{old}/c_{new} and, in order to avoid polarity of the latter, the last digit of the new z coordinate has been adjusted so as to secure twofold symmetry in the separate layers.

The new coordinates are given in table 8. Table 3 (columns 5 and 6) gives the coefficients $A_{ijklmnp}$ appropriate to equation (2) in order to generate the electrostatic energies of the expanded structures of table 8.

5. DISCUSSION

The discussion of the results derived from the calculations described in § 3 conveniently divides into six categories:

(a) Substitutional energies, U_{subs}

Some insight into the notional transformation energies of one silicate into another, without the usual accompanying structural changes, can be obtained from the differences of the lattice energies obtained from the hypothetical structure calculations. By using the results of table 4 (rounded to the nearest kJ mol^{-1}) we can obtain the energy differences, U_{subs} , listed in table 9.

Considering the table as consisting of sections, the upper left hand triangular trident concerns the conversion of trioctahedral micas into trioctahedral micas, the lower right hand triangular trident refers to dioctahedral \rightarrow trioctahedral conversion. Confining our attention to these sectors of the table, we can infer that insertion of an OH group (e.g. fluortalc \rightarrow talc, fluorphlogopite \rightarrow phlogopite) in a trioctahedral mica requires *ca.* 5527 kJ mol^{-1} , while replacement of Al in the tetrahedral Si_3Al group by Si to give Si_4 , with the consequent removal of a potassium interlayer cation in a trioctahedral structure, requires *ca.* 3440 kJ mol^{-1} (e.g. phlogopite \rightarrow talc, fluorphlogopite \rightarrow fluortalc). The situation for the dioctahedral trident is that OH insertion in a dioctahedral mica requires *ca.* 6721 kJ mol^{-1} (e.g. fluorpyrophyllite \rightarrow pyrophyllite, 1M Al fluormica \rightarrow 1M Al mica) while removal of KSi_3Al group and replacement by Si_4 requires *ca.* 3432 kJ mol^{-1} in the dioctahedral situation. The upper right hand 4×4 entries in table 9, concerning di \rightarrow trioctahedral and tri \rightarrow dioctahedral conversions, are now consistent with the above energies, provided that we assume that removal of Al from dioctahedral sites (X_2) and replacement by Mg in trioctahedral sites ($\text{X}_2\text{X}'$), generates *ca.* 4460 kJ mol^{-1} (e.g. 1M Al mica \rightarrow phlogopite, pyrophyllite \rightarrow talc) in the presence of a hydroxy group, while removal of Al from dioctahedral sites (X_2) and replacement by Mg in trioctahedral sites ($\text{X}_2\text{X}'$) generates *ca.* 3265 kJ mol^{-1} (e.g. fluorpyrophyllite \rightarrow fluortalc, 1M Al fluormica \rightarrow fluorphlogopite) in the absence of the OH group (fluorinated analogue). Table 10 summarizes these important conclusions. These estimates are, we imagine, predictively reliable but not quantitatively significant.

The remainder of the substitutional changes in table 9 can all be rationalized on the basis of table 10. Thus, to explain for example U_{subs} in the step 1M Al fluormica \rightarrow fluortalc we can consider it to be made up of the cycle shown in table 11.

If we compare the substitutional energies in table 11, in that they represent the process of pure site substitution without shift in the site positions, with actual changes taking place when a

TABLE 10. COMPONENTS OF SUBSTITUTIONAL ENERGY, U_{subs} OF TABLE 9/(kJ mol⁻¹)

substitution type	parent mica	daughter mica	U_{subs} energy required/(kJ mol ⁻¹)
F → OH	trioctahedral	trioctahedral	5527
F → OH	dioctahedral	dioctahedral	6721
KS ₃ Al → Si ₄	trioctahedral	trioctahedral	3444
KS ₃ Al → Si ₄	dioctahedral	dioctahedral	3432
Al ₂ → Mg ₃	dioctahedral	trioctahedral	4460
	hydroxy mica	hydroxy mica	
Al ₂ → Mg ₃	dioctahedral	trioctahedral	3265
	fluormica	fluormica	

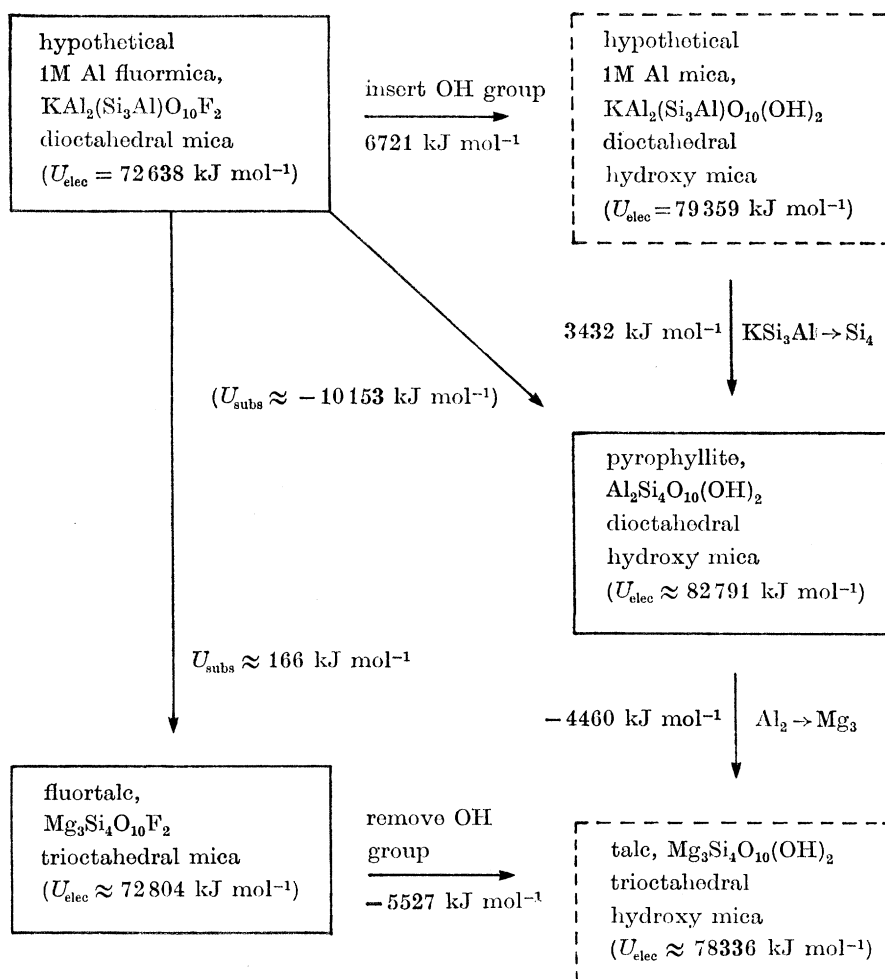
The magnitude of U_{subs} for the F → OH substitution can be rationalized by means of an approximate calculation. The substitution corresponds, effectively, to the addition of one H⁺ and one O⁻ attached to the nearest X' cation. Considering only nearest neighbours, the first contribution to U_{subs} corresponds to the interaction energy of H⁺ and O⁻ at a distance, r_{OH} , of 1.00 Å, the second contribution being the interaction energy of O⁻ and X' at a distance, $r_{\text{X'O}}$, of 1.917 Å. As there are two molecules in the unit cell, containing two (OH) groups, for the trioctahedral micas ($q_{\text{X}'} = 2$):

$$2(1/r_{\text{OH}} + 2/r_{\text{X'O}}) = 4.043e^2\text{Å}^{-1} = 5617 \text{ kJ mol}^{-1}.$$

For the dioctahedral micas, $q_{\text{X}'} = 3$ and so the energy becomes

$$2(1/r_{\text{OH}} + 3/r_{\text{X'O}}) = 5.130e^2\text{Å}^{-1} = 7127 \text{ kJ mol}^{-1}.$$

This crude approximation compares favourably with the values found in the above table, showing that the total contribution of the other ions is relatively small.

TABLE 11. RATIONALIZATION OF SUBSTITUTIONAL ENERGIES: 1M Al
FLUORMICA → PYROPHYLLITE

particular generic structure converts to another *true* structure, we can interpret the differences as being due to the relaxation energy of the structure change (the energy change caused by changes in site positions).

Before proceeding to such a discussion in the next subsection, it is instructive to ask how well one can predict the lattice energies of the substitutionally derivable structures from calculations on the single (most fully substituted) structure with all possible site positions being assigned generalized charges, and parameterizing an equation of the form of (2). Tables 12 and 13 give this information.

TABLE 12. COMPARISON OF ELECTROSTATIC ENERGY CALCULATIONS FOR HYPOTHETICALLY DERIVED STRUCTURES, FOR TRUE STRUCTURES AND FROM RESULTS OF GIESE'S (1975*a*) CALCULATIONS

silicate	U_{elec} (Giese 1975 <i>a</i>)	$U_{\text{elec}} (= U_{\text{true}})$		predicted $U_{\text{elec}} (= U_{\text{hyp}})$	
		calculated from literature structures (table 5)	% difference w.r.t. Giese	derived from generic structure by adiabatic substitutional scheme (table 1)	% difference w.r.t. Giese
talc	79688†	79599	0.11	78336§	1.70
fluortalc	73052†	73099	0.00	72805§	0.34
pyrophyllite	83203†	83337	0.16	82792§	0.50
fluorpyrophyllite	76223†	76348	0.16	76066§	0.20
1M Al mica	—	79359	—	79356	—
1M Al fluormica	—	72641	—	72638	—
phlogopite	{ 74344‡ 74947†	— 74915	— 0.04	— 74892	— 0.07
fluorphlogopite	{ 68079‡ 68533†	— 68645	— 0.16	— 69369¶	— 1.22

† Structure corresponds with that taken in present study (table 5).

‡ Structure taken from Joswig (1972).

§ Triclinic symmetry possessed by true structure not accounted for by calculation which assumes monoclinic symmetry of parent hypothetical structure (table 2)

|| OH group orientation in true structure differs from that of hypothetical structure.

¶ True structure differs from hypothetical structure because of size of octahedra and tilting and rotation of tetrahedra.

Table 12 shows that for the minerals talc, fluortalc, pyrophyllite, fluorpyrophyllite, phlogopite and fluorphlogopite, assuming the atomic sites to possess valence charges (i.e. $q_{\text{K}} = 1$, $q_{\text{Si}} = 4$, $q_{\text{Al}} = 3$, $q_{\text{O}'} = -2$, $q_{\text{H}} = 1$, $q_{\text{F}} = -1$, etc.), then the U_{elec} values for the true structures correspond on average to within about 0.1% of the Giese values (maximum difference found = 0.16%), while the predicted lattice energies from the single calculations correspond, on average, to within 0.7% of the Giese values (with a maximum discrepancy of 1.7% for talc for which two relaxation effects are not taken into account). Such small differences are, of course, highly satisfactory, and give us confidence to extend our lattice energy predictions to the other minerals in table 1 with hope of reasonable quantitative reliability.

Table 13 shows a comparison of Slaughter's (1966) calculations of U_{elec} for pyrophyllite and talc with our values, derived from equation (2) with the Slaughter charges ($q_{\text{Al}} = 1.9$, $q_{\text{Si}} = 2.05$, $q_{\text{O}'} = -1.145$, $q_{\text{O}} = -1.025$, $q_{\text{H}} = 0.0$ or 0.39 for pyrophyllite; $q_{\text{Al}} = 1.46$, $q_{\text{Si}} = 2.05$, $q_{\text{O}'} = -1.234$, $q_{\text{O}} = -1.025$, $q_{\text{H}} = 0.0$ or 0.39 for talc). We believe the coulombic energy, E_{c} , quoted by Slaughter, actually corresponds to $2U_{\text{elec}}$ rather than to U_{elec} because Slaughter's molecular formulae correspond to $\text{AlSi}_2\text{O}_5(\text{OH})$ for pyrophyllite and $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})$ for talc.

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TABLE 13. COMPARISON OF ELECTROSTATIC ENERGY CALCULATIONS WITH SLAUGHTER'S CHARGES IN EQUATION (2) OF THIS PAPER WITH VALUES QUOTED IN SLAUGHTER (1966)

mineral	author	structure used	charges	$U_{\text{elec}}/$ (kJ mol ⁻¹)
pyrophyllite H ^{+0.00}	Slaughter	Gruner (1934) Hendricks (1938) ($a = 5.16 \text{ \AA}$, $b = 8.90 \text{ \AA}$, $c = 18.64 \text{ \AA}$)	$q_{\text{Al}} = 1.9$ $q_{\text{Si}} = 2.05$ $q_{\text{O}} = -1.025$ $q_{\text{O}'} = -1.145$ $q_{\text{H}} = 0.0$	22 131
pyrophyllite H ^{+0.00}	Jenkins and Hartman	Wardle & Brindley (1972) ($a = 5.16 \text{ \AA}$, $b = 8.957 \text{ \AA}$, $c = 9.351 \text{ \AA}$)	$q_{\text{Al}} = 1.9$ $q_{\text{Si}} = 2.05$ $q_{\text{O}} = -1.025$ $q_{\text{O}'} = -1.145$ $q_{\text{H}} = 0.0$	27 222
pyrophyllite H ^{+0.39}	Slaughter	Gruner (1934) Hendricks (1938)	$q_{\text{Al}} = 1.9$ $q_{\text{Si}} = 2.05$ $q_{\text{O}} = -1.025$ $q_{\text{O}'} = -1.145$ $q_{\text{H}} = 0.39$	23 551
pyrophyllite H ^{+0.39}	Jenkins and Hartman	Wardle & Brindley (1972)	$q_{\text{Al}} = 1.9$ $q_{\text{Si}} = 2.05$ $q_{\text{O}} = -1.025$ $q_{\text{O}'} = -1.145$ $q_{\text{H}} = 0.39$	27 931
talc H ^{+0.00}	Slaughter	Gruner (1934) Hendricks (1938) ($a = 5.28 \text{ \AA}$, $b = 9.15 \text{ \AA}$, $c = 18.92 \text{ \AA}$)	$q_{\text{Mg}} = 1.46$ $q_{\text{Si}} = 2.05$ $q_{\text{O}} = -1.025$ $q_{\text{O}'} = -1.234$ $q_{\text{H}} = 0.0$	23 017
talc H ^{+0.00}	Jenkins and Hartman	Raynor & Brown (1973) ($a = 5.29 \text{ \AA}$, $b = 9.179 \text{ \AA}$, $c = 9.496 \text{ \AA}$)	$q_{\text{Mg}} = 1.46$ $q_{\text{Si}} = 2.05$ $q_{\text{O}} = -1.025$ $q_{\text{O}'} = -1.234$ $q_{\text{H}} = 0.0$	32 257
talc H ^{+0.39}	Slaughter	Gruner (1934) Hendricks (1938)	$q_{\text{Mg}} = 1.46$ $q_{\text{Si}} = 2.05$ $q_{\text{O}} = -1.025$ $q_{\text{O}'} = -1.234$ $q_{\text{H}} = 0.39$	24 597
talc H ^{+0.39}	Jenkins and Hartman	Raynor & Brown (1973)	$q_{\text{Mg}} = 1.46$ $q_{\text{Si}} = 2.05$ $q_{\text{O}} = -1.025$ $q_{\text{O}'} = -1.234$ $q_{\text{H}} = 0.39$	22 992

Slaughter's results are clearly at variance with our results, and the differences would seem to be too large to be attributable solely to the differences in crystal structure data employed (cf Giese's calculations on phlogopite with the Joswig (1972) and the McCauley *et al.* (1973) structures where U_{elec} differs by 603 kJ mol⁻¹). The present difference (U_{elec} (Slaughter) - U_{elec} (Jenkins)) is between 760 and 5091 kJ mol⁻¹.

The effect (in going from the structures with $q_{\text{H}} = 0$ to those with $q_{\text{H}} = 0.39$) of hydrogen atom

addition in pyrophyllite is calculated to be 709 kJ mol^{-1} (Jenkins & Hartman) and 420 kJ mol^{-1} (Slaughter), and in talc to be 735 kJ mol^{-1} (Jenkins & Hartman) and 1580 kJ mol^{-1} (Slaughter). While our values for this process of 'charging up' the hydrogen are of similar magnitude in the two phyllosilicates, as might be predicted, Slaughter's values are widely different from one another. This may be a feature of the use of the very much older structural data of Gruner (1934) in the case of Slaughter's calculations. It must be recognized, of course, that this was the only structural data available in 1963.

As further confirmation of the reliability of our results, we can turn to the work of Appelo (1977), whose results for U_{elec} for phlogopite and its fluorinated analogue are cited in Table 14.

TABLE 14. COMPARISON OF ELECTROSTATIC ENERGY CALCULATION FOR TRUE PHLOGOPITE AND FLUORPHLOGOPITE FROM THESE STUDIES AND THOSE OF APPELO

silicate	Appelo (1978) $U_{\text{elec}}/(\text{kJ mol}^{-1})$	this work $U_{\text{elec}}/(\text{kJ mol}^{-1})$	percentage difference
phlogopite	70 087	74 915	6.4†
fluorphlogopite	68 643	68 645	0.0

† It should be noted that in the case of phlogopite the structure used by Appelo (1978) was that of Joswig (1972) whereas in our case we employed the McCauley *et al.* (1973) structure derived from fluorphlogopite. As regards the charges Appelo uses ($q_{\text{K}} = 0.92$, $q_{\text{Mg}} = 2.025$, $q_{\text{O}} = -2$, $q_{\text{T}} = 3.7275$ and $q_{\text{H}} = 0.485$) whereas in our calculations valence charges were used ($q_{\text{K}} = 1$, $q_{\text{Mg}} = 2$, $q_{\text{O}} = -2$, $q_{\text{T}} = 3.75$ and $q_{\text{H}} = 1.0$) in the case of phlogopite. Identical charges were chosen by both workers for fluorphlogopite.

Once again, as with Giese's calculation, we establish perfect agreement in the case of fluorphlogopite where both calculations adopt the same structural data and assign the same valence charges. In the case of phlogopite, Giese has calculated the difference between the Joswig and McCauley structures (table 12) to be 603 kJ mol^{-1} when isovalent charges are employed for both structures. The considerable difference, amounting to some 4828 kJ mol^{-1} , between the calculation of Appelo and this work for phlogopite must therefore stem from the differences in the electrostatic terms involving K, Mg, T and H which take differing charges in the true calculations and from the structural difference. We can, of course, check this supposition with equation (16), since we calculate that

$$U_{\text{elec}} (\text{phlogopite: McCauley structure: } q_{\text{K}} = 0.92, q_{\text{T}} = 0.485, q_{\text{Mg}} = 2.025, \\ q_{\text{T}} = 3.7275, q_{\text{O}} = -2, q_{\text{O}'} = -1.4375) = 70541 \text{ kJ mol}^{-1} \quad (17)$$

Thus,

$$\begin{array}{ccccc} \text{phlogopite} & \xrightarrow{\text{Joswig}} & \text{phlogopite} & \xrightarrow{\text{McCauley}} & \text{phlogopite} \\ & \text{571 kJ mol}^{-1} & & \text{4374 kJ mol}^{-1} & \\ & \text{(valence charges)} & & \text{(valence charges)} & \text{(Appelo charges)} \\ & \text{(} U_{\text{elec}} = 74344 \text{ kJ mol}^{-1} \text{)} & & \text{(} U_{\text{elec}} = 74915 \text{ kJ mol}^{-1} \text{)} & \text{(} U_{\text{elec}} = 70541 \text{ kJ mol}^{-1} \text{)} \end{array}$$

and we conclude that the difference in U_{elec} which can arise from the differing choice of charges is of the order of some 4300 kJ mol^{-1} , while that due to the differing structural parameters is of the order of 600 kJ mol^{-1} , amounting altogether to approximately 4900 kJ mol^{-1} , which is just the magnitude found. We therefore confirm that equation (16) is reliable for charges on phlogopite that differ from the valence charges.

(b) *Structural relaxation energies, U_{relax}*

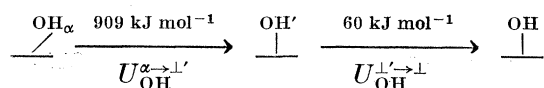
If we consider relaxation energies to be energy changes caused by alteration of orientation (by rotation or tilting) of the octahedra, U_{oct} , tetrahedra, U_{tet} , and of the OH groups, U_{OH} , and by the associated gross structural transitions, (for example, transformation of a monoclinic into a triclinic cell), then our treatment of generically derived structures when contrasted with the true calculations can give useful insight into the relative magnitudes of the above changes.

If we represent a hydroxy mica structure having the OH group orientation at an angle θ to the normal to the interlayer by the symbol $\frac{\text{OH}_\theta}{/}$, and the structure where the OH group is normal to the interlayer surface by the symbol $\frac{\text{OH}}{\perp}$, with $U_{\text{OH}}^{\theta \rightarrow \perp}$ representing the energy difference we can analyse the results of hypothetical calculations and true calculations of tables 7 and 4 so as to extract relaxation (electrostatic) energy data. Table 15 summarizes the information we can obtain for the relaxation energy of various structures, U_{relax} , as calculated from the difference of U_{true} and U_{hyp} for calculations already described in this paper.

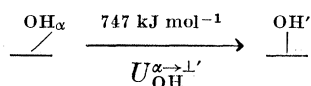
In general terms, as has been previously inferred, the electrostatic relaxation energies in table 15 rarely amount to more than 1.5% of the electrostatic lattice energies of the individual silicates.

(i) *Hydroxyl relaxation energies, U_{OH}*

If we consider the way in which the fluorinated analogues are constituted from the hydroxylated silicates (i.e. by placing the fluorine atoms at the hydroxyl oxygen positions without further change in structure) it will be clear that the difference between the relaxation energies calculated from hydroxyl as opposed to fluorine derivatives can be attributed solely to changes in hydroxyl orientations in the silicates. Accordingly, from table 15, we can extract the following information for the changes in OH orientation as influenced by various environments. In table 15 we have represented the hydroxyl orientations of talc and phlogopite as $\frac{\text{OH}}{\perp}$ and $\frac{\text{OH}'}{\perp}$ (being known to be approximately perpendicular to the layer) and those of 1M Al mica and pyrophyllite as $\frac{\text{OH}_\alpha}{/}$ and $\frac{\text{OH}}{/}$ respectively. For the trioctahedral silicate talc (without an interlayer cation) we find:



For phlogopite, a trioctahedral silicate having interlayer K^+ cations



The influence of the K^+ ion is not very large. Giese (1971), in his electrostatic calculations on the position of the H^+ ion in the dioctahedral mica muscovite, found OH angles differing by some 10° depending on whether K^+ ions were present or not. More recently it has been stated (Datta & Giese 1973) that in muscovite the OH is at 12° to the cleavage plane while without the interlayer K^+ the angle increases to 53° . The trioctahedral minerals talc and phlogopite have

TABLE 15. CALCULATED RELAXATION ENERGIES, U_{relax} CALCULATED FROM DIFFERENCES IN LATTICE ENERGIES OF TRUE AND GENERIC STRUCTURES

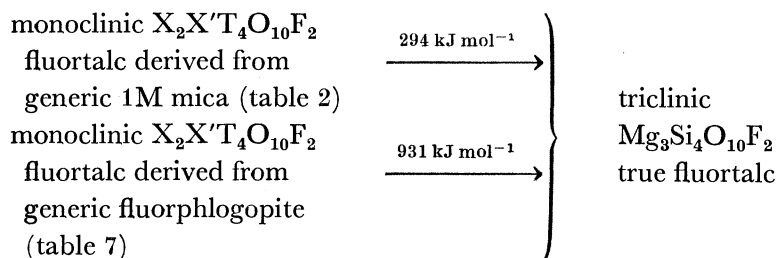
silicate	generic structure	$U_{\text{hyp}}/$ (kJ mol ⁻¹)	true structure	$U_{\text{true}}/$ (kJ mol ⁻¹)	$U_{\text{relax}}/$ (kJ mol ⁻¹)
talc	1M mica (table 2) $X_2X'T_4O_{10}(OH)_2$ OH _α /	78 336	$Mg_3Si_4O_{10}(OH)_2$ OH 	79 599	1263
	monoclinic		triclinic		
fluortalc	1M mica (table 2) $X_2X'T_4O_{10}F_2$ monoclinic	72 805	$Mg_3Si_4O_{10}F_2$ triclinic	73 099	294
pyrophyllite	1M mica (table 2) $X_2T_4O_{10}(OH)_2$ OH _α /	82 792	$Al_2Si_4O_{10}(OH)_2$ OH _β /	83 337	545
	monoclinic		triclinic		
fluorpyrophyllite	1M mica (table 2) $X_2T_4O_{10}F_2$ monoclinic	76 066	$Al_2Si_4O_{10}F_2$ triclinic	76 348	282
phlogopite	1M mica (table 2) $KX_2X'T_4O_{10}(OH)_2$ OH _α /	74 892	$KMg_3(Si_3Al)O_{10}(OH)_2$ OH' 	74 915	23
	monoclinic		monoclinic		
fluorphlogopite	1M mica (table 2) $KX_2X'T_4O_{10}F_2$ monoclinic	69 369	$KMg_3(Si_3Al)O_{10}F_2$ monoclinic	68 645	-724
pyrophyllite	talc (table 7) $X_2Si_4O_{10}(OH)_2$ OH 	83 673	$Al_2Si_4O_{10}(OH)_2$ OH _β /	83 337	-336
	triclinic		triclinic		
fluorpyrophyllite	talc (table 7) $X_2Si_4O_{10}F_2$ triclinic	75 147	$Al_2Si_4O_{10}F_2$ triclinic	76 348	1201
talc	phlogopite (table 7) $KX_2X'(Si_3Al)O_{10}(OH)_2$ OH' 	78 608	$Mg_3Si_4O_{10}(OH)_2$ OH 	79 599	991
	monoclinic		triclinic		
fluortalc	phlogopite (table 7) $KX_2X'(Si_3Al)O_{10}F_2$ monoclinic	72 168	$Mg_3Si_4O_{10}F_2$ triclinic	73 099	931

their OH groups perpendicular to the interlayer and as shown above these orientations are the most stable ones. Yet Juo & White (1969) have shown that in films of biotite (Fe-bearing phlogopite), the OH orientation depends on the oxidation states of the octahedral Fe atoms. This may be ascribed to the distortion of the more or less trigonal symmetry of the electrostatic field around the OH group in phlogopite or non-oxidized biotite.

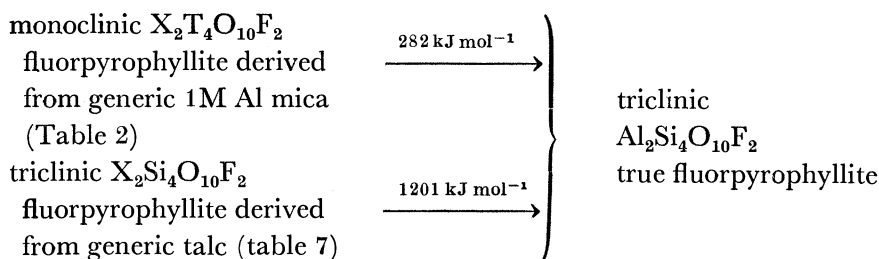
(ii) *Tetrahedral and octahedral relaxation energies, U_{tet} and U_{oct}*

In general terms the silicates discussed in this paper and for which structural data is available, are such that those possessing the Si_3Al group (with the associated interlayer cation) at the tetrahedral site have monoclinic symmetry while those having the Si_4 group at the tetrahedral site exhibit triclinic symmetry. This observation is not influenced by the dioctahedral or trioctahedral character of the silicate in question and seems to imply that the tetrahedral relaxation energies should in general be larger than the corresponding octahedral ones.

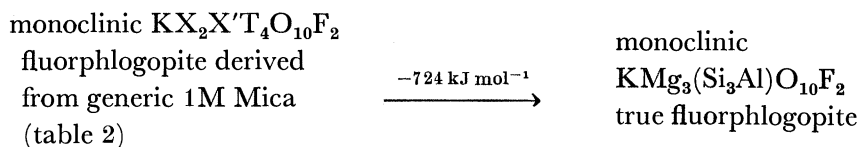
From the information given in table 15 for the fluorinated silicates we find that the relaxation energies for fluortalc are



the relaxation energies for fluorpyrophyllite are



and the relaxation energy for fluorphlogopite is



In the fluortalc transformation, the derived 1M mica structure has the dioctahedral arrangement of 1M Al mica with an extra octahedron added to form a trioctahedral generic structure; we label it ddt. On converting to fluortalc (true structure) the octahedral positions are those of a true trioctahedral mica (talc), denoted ttt. The tetrahedral arrangement in the generic compound 1M mica is as for Si_3Al tetrahedra (denoted T), while in the talc the tetrahedra are Si_4 type (denoted Si). We can denote the conversion of fluortalc (generic 1M mica) to true fluortalc as

$$U_{\text{oct}}(\text{ddt} \rightarrow \text{ttt}) + U_{\text{tet}}(\text{T} \rightarrow \text{Si}) = 294 \text{ kJ mol}^{-1}. \quad (18)$$

The generic phlogopite (table 7) possesses trioctahedral symmetry (ttt) and hence the transformation to fluortalc is written as

$$U_{\text{oct}}(\text{ttt} \rightarrow \text{ttt}) + U_{\text{tet}}(\text{T} \rightarrow \text{Si}) = 931 \text{ kJ mol}^{-1}, \quad (19)$$

with a similar tetrahedral rearrangement as before.

In the fluorpyrophyllite case, the true fluorpyrophyllite is dioctahedral (denoted dd) and so the conversion from 1M mica (ddt) (the trioctahedral position t not being occupied) can be written as

$$U_{\text{oct}}(\text{dd} \rightarrow \text{dd}) + U_{\text{tet}}(\text{T} \rightarrow \text{Si}) = 282 \text{ kJ mol}^{-1}. \quad (20)$$

The fluorpyrophyllite derived from generic talc has trioctahedral sites occupied at two positions (tt), and the transformation to true fluorpyrophyllite can be written as

$$U_{\text{oct}}(\text{tt} \rightarrow \text{dd}) = 1201 \text{ kJ mol}^{-1}. \quad (21)$$

Since both tetrahedral sites are of the Si_4 type, and since both structures are triclinic, although with small differences, we suppose that the energy involved in a slight tetrahedral rearrangement can be neglected.

In the fluorphlogopite transformation, fluorphlogopite derived from generic 1M mica (ddt) goes to trioctahedral fluorphlogopite (ttt) with no tetrahedral rearrangement:

$$U_{\text{oct}}(\text{ddt} \rightarrow \text{ttt}) = -724 \text{ kJ mol}^{-1}. \quad (22)$$

From equations (17), (18), (19), (20) and (21) we conclude that

$$U_{\text{tet}}(\text{T} \rightarrow \text{Si}) = 1018 \text{ kJ mol}^{-1}, \quad (23)$$

which confirms the contention made above that the tetrahedral rearrangement is the largest relaxation energy and, indeed, is responsible for the monoclinic \rightarrow triclinic symmetry changes evident in the above transformations. For the octahedral rearrangements, with the notation above, we find:

$$U_{\text{oct}}(\text{ddt} \rightarrow \text{ttt}) = -724 \text{ kJ mol}^{-1}, \quad (24)$$

$$U_{\text{oct}}(\text{dd} \rightarrow \text{dd}) = -736 \text{ kJ mol}^{-1}, \quad (25)$$

$$U_{\text{oct}}(\text{tt} \rightarrow \text{dd}) = 1201 \text{ kJ mol}^{-1}, \quad (26)$$

$$U_{\text{oct}}(\text{ttt} \rightarrow \text{ttt}) = -87 \text{ kJ mol}^{-1}. \quad (27)$$

From these values, we conclude that the electrostatic component of U_{oct} amounts to -736 kJ mol^{-1} for the transition from monoclinic to triclinic dioctahedral micas. For trioctahedral micas, the same transition involves a U_{oct} of -87 kJ mol^{-1} . The other values are associated with the transition from trioctahedral to dioctahedral micas. In dioctahedral micas, two octahedra are filled and have small dimensions, while the third octahedron is empty and is relatively large. The octahedra in trioctahedral micas are all filled and have dimensions somewhere between the small and large octahedra, i.e. they are medium-sized.

Equation (21) refers to the transition of three medium-sized octahedra, of which two are occupied by Al, to two small and one large octahedra. This change is accompanied by an increase in energy of 1200 kJ mol^{-1} , so we could say that the change of one medium to one small octahedron gives an increase of 600 kJ mol^{-1} for Al. For Mg this change is then presumably $\frac{2}{3}$ of it, being 400 kJ mol^{-1} . Equation (22) states that the transition of three medium octahedra filled with Mg to two small and one large octahedron gives an increase of 724 kJ mol^{-1} . The contraction of

two medium octahedra to two small octahedra would give 800 kJ mol⁻¹, so the expansion of one medium to one large octahedron would give -76 kJ mol⁻¹. These electrostatic values seem to be reasonable: the contraction of a MgO₄F₂ octahedron with a cation-anion distance of 2.06 Å to 1.91 Å, taking the charges on the oxygen as -1 because they all belong to two octahedra, affords 636 kJ mol⁻¹ per Mg.

(c) *Site potentials*

The site potentials V_j for the individual ions j in a silicate, represent the potential required to remove the ions j from the crystal to infinity. For example, in fluorphlogopite KMg₃T₄O₁₀F₂ the site potentials of the individual ions are defined by the equations

$$V_K = [2Aq_K + Bq_K q_T + Cq_K q_{Mg} + Dq_K q_O + Eq_K q_F]/q_K, \quad (28)$$

$$V_T = [2Fq_T + Bq_K q_T + Gq_T q_{Mg} + Hq_T q_O + Jq_T q_F]/3.75q_T, \quad (29)$$

$$V_{Mg} = [2Kq_{Mg} + Lq_{Mg} q_O + Mq_{Mg} q_F + Cq_K q_{Mg} + Gq_T q_{Mg}]/3q_{Mg}, \quad (30)$$

$$V_O = [2Nq_O + Dq_K q_O + Hq_T q_O + Lq_{Mg} q_O + Pq_O q_F]/10q_O, \quad (31)$$

$$V_F = [2Qq_F + Eq_K q_F + Jq_T q_F + Mq_{Mg} q_F + Pq_O q_F]/q_F, \quad (32)$$

where

$$U_{elec} = Aq_K^2 + Bq_K q_T + Cq_K q_{Mg} + Dq_K q_O + Eq_K q_F + Fq_T^2 + Gq_T q_{Mg} + Hq_T q_O + Jq_T q_F + Kq_{Mg}^2 + Lq_{Mg} q_O + Mq_{Mg} q_F + Nq_O^2 + Pq_O q_F + Qq_F^2, \quad (33)$$

which is precisely equivalent to the form of equation (2) so that, for example,

$$V_K = [2Aq_K + Bq_T + Cq_{Mg} + Dq_O + Eq_F] = \left(\frac{\partial U_{elec}}{\partial q_K} \right)_{q_{Mg}, q_T, q_O, q_F}. \quad (34)$$

As indicated above and in equation (3), our newly proposed expansion in the form equation (2) readily generates site potentials, V_j for a given ion j .

In table 16 we give some site potentials in e Å⁻¹, as calculated by Hartman using a direct Madelung summation for a few directions in fluorphlogopite, KMg₃(Si₃Al)O₁₀F₂.

TABLE 16. SITE POTENTIALS FOR FLUORPHLOGOPITE

ion	V_j (e Å ⁻¹) for face (hkl) in direction $[uvw]$			
	(200) [010]	(020) [100]	(001) [010]	(001) [100]
K	+0.837 236	+0.837 479	+0.836 054	+0.837 254
T	+3.155 194	+3.155 125	+3.153 162	+3.154 768
Mg ($y = 0.3306$)	+1.560 994	+1.560 818	+1.560 638	+1.560 751
Mg ($y = 0$)	+1.564 287	+1.564 198	+1.563 913	+1.564 034
O ($z = 0.1678$)	-1.994 514	-1.994 468	-1.996 467	-1.994 369
O ($z = 0.1682$)	-1.984 233	-1.984 081	-1.985 020	-1.984 236
O ($z = 0.3896$)	-1.952 321	-1.952 448	-1.952 808	-1.952 723
F	-0.904 646	-0.904 786	-0.905 120	-0.904 359

To illustrate the calculation of site potentials for fluorphlogopite from equation (2), we have

$$V_K = \left(\frac{\partial U_{elec}}{\partial q_K} \right)_{q_X, q_X', q_T, q_O, q_O'} = \sum_{i=0}^2 \sum_{j=0}^{(2-i)} \sum_{k=0}^{(2-j)} \sum_{l=0}^{(2-k)} \sum_{m=0}^{(2-l)} \sum_{n=0}^{(2-m)} i A_{ijklmnp} q_K^{i-1} q_X^j q_X'^k q_T^l q_O^m q_O'^n, \quad (35)$$

and, assuming $q_K = +1$, $q_X = q_{X'} = 2$, $q_T = 3.75$, $q_O = -2$ and $q_{O'} = -1$,

$$V_K = \sum_{i=0}^2 \sum_{j=0}^{(2-i)} \sum_{k=0}^{(2-j)} \sum_{l=0}^{(2-k)} \sum_{m=0}^{(2-l)} \sum_{n=0}^{(2-m)} (-1)^{m+n} i A_{ijklmnp} 3^{(j+k+l)} 5^{2(m-2l)}. \quad (36)$$

Similarly, for example,

$$V_F = \left(\frac{\partial U_{\text{elec}}}{\partial q_{O'}} \right)_{\substack{q_{O'}=q_F=-1 \\ q_K, q_X, q_{X'}, q_T, q_O}} = \sum_{i=0}^2 \sum_{j=0}^{(2-i)} \sum_{k=0}^{(2-j)} \sum_{l=0}^{(2-k)} \sum_{m=0}^{(2-l)} \sum_{n=0}^{(2-m)} n A_{ijklmnp} q_K^i q_X^j q_{X'}^k q_T^l q_O^m q_{O'}^n. \quad (37)$$

From equation (16) we have, putting $q_K = 1$, $q_T = 3.75$, $q_{Mg} = 2$, $q_O = -2$, $q_{O'} = -1$ and $q_H = 0$,

$$V_K = \left(\frac{\partial U_{\text{elec}}}{\partial q_K} \right)_{\substack{q_T, q_{Mg}, q_O, q_{O'} \\ q_H=0}} = [506.6q_K + 235.0q_T + 891.1q_{Mg} + 747.6q_O + 511.7q_{O'}] \quad (38)$$

$$= 1163 \text{ kJ mol}^{-1} \text{ e}^{-1} = 0.8372 \text{ e}\text{\AA}^{-1}, \quad (39)$$

assuming $1 \text{ e}^2 \text{\AA}^{-1} = 1389.3 \text{ kJ mol}^{-1}$. The corresponding F atom potential from equation (16) is

$$V_F = \left(\frac{\partial U_{\text{elec}}}{\partial q_{O'}} \right)_{\substack{q_K, q_{Mg}, q_T, q_O, q_{O'} \\ q_H=0}} = \frac{1}{2} [511.7q_K + 898.3q_T - 1436.1q_X + 1283.2q_O + 955.8q_{O'}] \quad (40)$$

$$= -1257.0 \text{ kJ mol}^{-1} \text{ e}^{-1} = -0.9048 \text{ e}\text{\AA}^{-1}. \quad (41)$$

Both V_K and V_F are in agreement with Hartman's (1979) independent calculations. Alternatively using our generic compound, we can calculate V_K and V_F from the coefficients from column 4 of table 2, for which

$$V_K = \left(\frac{\partial U_{\text{elec}}}{\partial q_K} \right)_{\substack{q_X, q_{X'}, q_T, q_O, q_{O'} \\ q_{O'}=-1 \\ q_H=0}} = [508.8q_K + 619.2q_X + 309.0q_{X'} + 276.2q_T + 795.8q_O + 524.2q_{O'}] \quad (42)$$

$$= 1285.1 \text{ kJ mol}^{-1} \text{ e}^{-1} = 0.925 \text{ e}\text{\AA}^{-1}, \quad (43)$$

and

$$V_F = \left(\frac{\partial U_{\text{elec}}}{\partial q_{O'}} \right)_{\substack{q_K, q_X, q_{X'}, q_T, q_O \\ q_H=0}} = \frac{1}{2} [524.2q_K - 1008.2q_X - 421.0q_{X'} + 833.9q_T + 1228.5q_O + 972.6q_{O'}] \quad (44)$$

$$= -1318.3 \text{ kJ mol}^{-1} \text{ e}^{-1} = -0.9489 \text{ e}\text{\AA}^{-1}. \quad (45)$$

In this latter case, V_T is given by

$$V_T = \left(\frac{\partial U_{\text{elec}}}{\partial q_T} \right)_{\substack{q_K, q_X, q_{X'}, q_O, q_{O'} \\ q_H=0}} = \frac{1}{3.75} [276.2q_K + 884.4q_X + 455.9q_{X'} + 3628.2q_T - 980.8q_O + 833.9q_{O'}] \quad (46)$$

$$= 17690.2 \text{ kJ mol}^{-1} \text{ e}^{-1} = 3.3955 \text{ e}\text{\AA}^{-1}, \quad (47)$$

so that although V_j calculated from the generic equation is slightly higher than the true site potential, the relative values are very nearly the same, for example,

$$\left(\frac{V_K^{\text{true}}}{V_T^{\text{true}}} \right) = 0.28; \quad \left(\frac{V_K^{\text{generic}}}{V_T^{\text{generic}}} \right) = 0.29. \quad (48)$$

The site potentials are easily generated from the basic coefficients $A_{ijklmnp}$ and are closely related to them.

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(d) Surface energies

Tables 17, 18 and 19 compare the lattice energies of the expanded structures for talc, pyrophyllite and phlogopite with the results of Giese (1975*a*). Equation (2) was parametrized for the 15 Å and 20 Å expanded 1M mica structures (table 8) derived from 1M Al mica, and the coefficients obtained are listed in table 3, columns 6 and 7.

TABLE 17. ELECTROSTATIC LATTICE ENERGIES FOR TALC, FLUORTALC AND EXPANDED ANALOGUES (TABLE 8) COMPARED WITH GIESE (1975*a*) CALCULATIONS

	$U_{elec}/(\text{kJ mol}^{-1})$			
	Jenkins			Giese's calculations
	table 6	table 7	equation (2) in the form of (4)	
talc (Raynor & Brown)	79599	—	—	79688
talc ($c = 10.139 \text{ \AA}$)	—	(78608)	—	—
talc ($c = 10.12 \text{ \AA}$)	—	—	78336	—
expanded talc (Raynor & Brown)	—	—	—	79671
expanded talc ($c = 15.32 \text{ \AA}$)	—	—	78341	—
expanded talc ($c = 20.24 \text{ \AA}$)	—	—	78343	—
fluortalc (Raynor & Brown)	73099	—	—	73052
fluortalc ($c = 10.139 \text{ \AA}$)	—	(72168)	—	—
fluortalc ($c = 10.12 \text{ \AA}$)	—	—	72805	—
expanded fluortalc (Raynor & Brown)	—	—	—	73035
expanded fluortalc ($c = 15.32 \text{ \AA}$)	—	—	72810	—
expanded fluortalc ($c = 20.24 \text{ \AA}$)	—	—	72812	—

TABLE 18. ELECTROSTATIC LATTICE ENERGIES FOR PYROPHYLLITE, FLUORPYROPHYLLITE AND EXPANDED ANALOGUES (TABLE 8) COMPARED WITH GIESE (1975*a*) CALCULATIONS

	$U_{elec}/(\text{kJ mol}^{-1})$			
	Jenkins			Giese's calculations
	table 6	table 7	equation (2) in the form of (5)	
pyrophyllite (Wardle & Brindley)	83337	—	—	83203
pyrophyllite ($c = 9.496 \text{ \AA}$)	—	(83673)	—	—
pyrophyllite ($c = 10.12 \text{ \AA}$)	—	—	82792	—
expanded pyrophyllite (Wardle & Brindley)	—	—	—	83176
expanded pyrophyllite ($c = 15.32 \text{ \AA}$)	—	—	82798	—
expanded pyrophyllite ($c = 20.24 \text{ \AA}$)	—	—	82800	—
fluorpyrophyllite (Wardle & Brindley)	76348	—	—	76223
fluorpyrophyllite ($c = 9.496 \text{ \AA}$)	—	(75147)	—	—
fluorpyrophyllite ($c = 10.12 \text{ \AA}$)	—	—	76066	—
expanded fluorpyrophyllite (Wardle & Brindley)	—	—	—	76196
expanded fluorpyrophyllite ($c = 15.32 \text{ \AA}$)	—	—	76072	—
expanded fluorpyrophyllite ($c = 20.24 \text{ \AA}$)	—	—	76073	—

For 1M Al mica and 1M Al fluormica (not calculated by Giese) we obtain the results in table 4.

The results for the surface energy of the phyllosilicates treated by Giese (1975*a*) comprise the data given in Table 20.

It should be noted that the F and OH analogues have exactly the same atomic positions: the only difference is the extra H^+ ion.

TABLE 19. ELECTROSTATIC LATTICE ENERGIES OF PHLOGOPITE, FLUORPHLOGOPITE AND EXPANDED ANALOGUES (TABLE 8) COMPARED WITH GIESE'S (1975*a*) CALCULATIONS

	$U_{\text{elec}}/(\text{kJ mol}^{-1})$		
	Jenkins		Giese's calculations
	equation (16)	equation (2) in the form of (7)	
phlogopite (OH) (McCauley)	74915	—	74947
phlogopite (OH) (Joswig)	—	—	74344
phlogopite (OH) $c = 10.12 \text{ \AA}$	—	74892	—
expanded phlogopite (OH) (McCauley)	—	—	74857
expanded phlogopite (OH) (Joswig)	—	—	74250
expanded phlogopite (OH) $c = 15.32 \text{ \AA}$	—	74671	—
expanded phlogopite (OH) $c = 20.24 \text{ \AA}$	—	74672	—
fluorphlogopite (McCauley)	68645	—	68533
fluorphlogopite (Joswig)	—	—	68079
fluorphlogopite $c = 10.12 \text{ \AA}$	—	69369	—
expanded fluorphlogopite (McCauley)	—	—	68420
expanded fluorphlogopite (Joswig)	—	—	67964
expanded fluorphlogopite $c = 15.32 \text{ \AA}$	—	69148	—
expanded fluorphlogopite $c = 20.24 \text{ \AA}$	—	69148	—

TABLE 20. SURFACE ENERGIES FOR PHYLLOSILICATES

mineral		surface energy
dioctahedral muscovite $2M_1$ (based on Rothbauer (1971) structure)	$\text{KAl}_2\text{T}_4\text{O}_{10}\text{F}_2$ $\text{KAl}_2\text{T}_4\text{O}_{10}(\text{OH})_2$	136.4 kJ mol ⁻¹ 134.7 kJ mol ⁻¹
dioctahedral pyrophyllite (based on Wardle & Brindley (1972) structure)	$\text{Al}_2\text{Si}_4\text{O}_{10}\text{F}_2$ $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$	27.6 kJ mol ⁻¹ 27.3 kJ mol ⁻¹
trioctahedral phlogopite (based on Joswig (1972) structure)	$\text{KMg}_3\text{T}_4\text{O}_{10}\text{F}_2$ $\text{KMg}_3\text{T}_4\text{O}_{10}(\text{OH})_2$	115.4 kJ mol ⁻¹ 93.7 kJ mol ⁻¹
trioctahedral phlogopite (based on McCauley <i>et al.</i> (1973) structure)	$\text{KMg}_3\text{T}_4\text{O}_{10}\text{F}_2$ $\text{KMg}_3\text{T}_4\text{O}_{10}(\text{OH})_2$	113.8 kJ mol ⁻¹ 89.5 kJ mol ⁻¹
trioctahedral talc (based on Raynor & Brown (1973) structure)	$\text{Mg}_3\text{Si}_4\text{O}_{10}\text{F}_2$ $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	17.3 kJ mol ⁻¹ 17.5 kJ mol ⁻¹

The values of the experimentally determined cleavage energies show rather large variations. Gutshall *et al.* (1970) find 3630 mJ m⁻² for natural phlogopite and 6060 mJ m⁻² for synthetic phlogopite, both in high vacuum. In air the values are 700 mJ m⁻² and 500 mJ m⁻² respectively. These high values presumably arise because the interlayer potassium ions do not divide themselves equally on both sides of the cleavage plane, thus charging the flakes. Taking into account this charging Metzlik & Afanas'eva (1973) obtain 380 mJ m⁻². They did not specify the mica, but if we assume that the mica involved was muscovite, this cleavage energy corresponds to a surface energy of 107 kJ mol⁻¹, which compares favourably with the values calculated by Giese for phlogopite.

As pointed out above, Giese's values are based on an ordered arrangement of the K⁺ ions on the surface. Our calculations are based on the hypothesis that the K⁺ ions are statistically divided between the two surfaces and so we gave each K⁺ ion a charge $\frac{1}{2}q_{\text{K}}$. In appendix 1 we describe the procedure to correct for this difference. For fluorphlogopite this correction amounts to -92 kJ mol⁻¹. Since this correction term will not change very much in going from one potassium mica to another, this value should also hold for phlogopite, 1M Al mica and 1M Al fluormica.

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TABLE 21. ENERGY DIFFERENCE, ΔU , BETWEEN THE LATTICE ENERGY OF BASIC CONTRACTED STRUCTURE AND LATTICE ENERGY OF EXPANDED STRUCTURE

	$U_{\text{contracted structure}}$ (kJ mol ⁻¹)	$U_{\text{expanded structure}}/(\text{kJ mol}^{-1})$		$\Delta U/(\text{kJ mol}^{-1})$
		15 Å	20 Å	
phyllosilicate	ca. 10 Å			
1M Al mica	79355	79136	79136	+ 219
phlogopite	74892	74671	74672	+ 220
talc	78336	78341	78343	- 7
pyrophyllite	82792	82798	82800	- 8
beidellite	82422	82429	82431	- 9
illite	79673	79499	79499	+ 174
1M fluormica	72638	72417	72417	+ 221
fluorphlogopite	69369	69148	69148	+ 221
fluortalc	72805	72810	72812	- 7
fluorpyrophyllite	76066	76072	76073	- 7
fluorbeidellite	75697	75704	75705	- 8
fluorillite	72954	72780	72780	+ 174

Table 21 gives the energy difference, ΔU , between the expanded micas and their basic structures. It is seen that for the potassium micas $\Delta U = 220 \text{ kJ mol}^{-1}$, which becomes, on correction, 128 kJ mol^{-1} . As shown in the appendix, the Madelung method applied to fluorphlogopite leads to a value of 109 kJ mol^{-1} which compares astonishingly well with the experimental value of Metzlik & Afanas'eva (1973). Table 21 gives the energy difference, ΔU , between the expanded micas and their basic structures:

$$\Delta U = U_{\text{basic}} - U_{\text{expanded}}, \quad (49)$$

$$\Delta U = \sum_{i=0}^2 \sum_{j=0}^{(2-i)} \sum_{k=0}^{(2-j)} \sum_{l=0}^{(2-k)} \sum_{m=0}^{(2-l)} \sum_{n=0}^{(2-m)} \sum_{p=0}^{(2-n)} (A_{ijklmnp}^{\text{basic}} - A_{ijklmnp}^{\text{expanded}}) q_{\text{K}}^i q_{\text{X}}^j q_{\text{X}}^k q_{\text{T}}^l q_{\text{O}}^m q_{\text{H}}^n. \quad (50)$$

Thus for example, for pyrophyllite, ΔU can be written as

$$\Delta U = \sum_{j=0}^2 \sum_{l=0}^{(2-j)} \sum_{m=0}^{(2-k)} \sum_{n=0}^{(2-l)} \sum_{p=0}^{(2-m)} (-1)^m 3^j 2^{(2l+m)} \{A_{j0lmp}^{\text{basic}} - A_{j0lmp}^{\text{expanded}}\} q_{\text{O}}^n q_{\text{H}}^p. \quad (51)$$

if we use $A_{j0lmp}^{\text{expanded}}$ coefficients calculated from the 15 Å expanded mica (table 3, column 5), A_{j0lmp}^{basic} being taken from table 3 (column 4), we have

$$\begin{aligned} \Delta U_{\text{pyrophyllite}} = & 637.2q_{\text{Al}}^2 + 1815.3q_{\text{Al}}q_{\text{Si}} + 4617.0q_{\text{Al}}q_{\text{O}} + 1219.6q_{\text{Al}}q_{\text{O}'} + 1194.5q_{\text{Al}}q_{\text{H}} \\ & + 1079.3q_{\text{Si}}^2 + 5557.2q_{\text{Si}}q_{\text{O}} + 1704.8q_{\text{Si}}q_{\text{O}'} + 1656.0q_{\text{Si}}q_{\text{H}} \\ & + 7145.1q_{\text{O}}^2 + 4341.2q_{\text{O}}q_{\text{O}'} + 4218.8q_{\text{O}}q_{\text{H}} + 581.9q_{\text{O}}^2 \\ & + 1138.6q_{\text{O}'}q_{\text{H}} + 557.3q_{\text{H}}^2, \end{aligned} \quad (52)$$

which reduces to the equation

$$\Delta U_{\text{pyrophyllite}} = -5.7 - 0.5q_{\text{H}} + 0.6q_{\text{H}}^2 \quad (53)$$

under the substitution ($q_{\text{Al}} = +3$, $q_{\text{Si}} = +4$, $q_{\text{O}} = -2$, $q_{\text{O}'} = -(1 + q_{\text{H}})$).

If we use $A_{j0lmp}^{\text{expanded}}$ coefficients calculated from the 20 Å expanded mica (table 3, column 6) with the same A_{j0lmp}^{basic} coefficients from column 4, we find

$$\begin{aligned} \Delta U_{\text{pyrophyllite}} = & 1240.5q_{\text{Al}}^2 + 3879.5q_{\text{Al}}q_{\text{Si}} + 9820.7q_{\text{Al}}q_{\text{O}} + 2399.4q_{\text{Al}}q_{\text{O}'} \\ & + 2363.4q_{\text{Al}}q_{\text{H}} + 2797.2q_{\text{Si}}^2 + 14223.3q_{\text{Si}}q_{\text{O}} + 3716.8q_{\text{Si}}q_{\text{O}'} \\ & + 3644.8q_{\text{Si}}q_{\text{H}} + 18077.6q_{\text{O}}^2 + 9413.0q_{\text{O}}q_{\text{O}'} + 9232.9q_{\text{O}}q_{\text{H}} \\ & + 1158.7q_{\text{O}}^2 + 2281.4q_{\text{O}'}q_{\text{H}} + 1122.7q_{\text{H}}^2, \end{aligned} \quad (54)$$

which reduces to the equation

$$\Delta U_{\text{pyrophyllite}} = -7.2 + 0.2q_{\text{H}} \quad (55)$$

under the substitution ($q_{\text{Al}} = +3$, $q_{\text{Si}} = +4$, $q_{\text{O}} = -2$ and $q_{\text{O}'} = -(1 + q_{\text{H}})$). These equations (46) and (48) give the ΔU values in table 21.

We can now compare the results of table 21 for the surface energies of the hypothetical structures with those of Giese given earlier for the true structures. Let us consider first table 21. Three conclusions are evident:

(a) The surface energies are the same for hydroxyl and for fluormicas. We should bear in mind that the OH group was supposed to make an angle of 78° with the normal of the silicate layer. In order to determine the maximum influence of the OH to F substitution on the surface energy, we made the following calculation. In the true structure of fluorphlogopite an O^{2-} ion was placed at the F^{-1} site, and a H^+ ion at the position (0.1010, 0.0000, 0.3097), giving an OH group perpendicular to the layer. Since the substitution involves only the addition of a charge of -1 on the F site and a charge of $+1$ on the H site, we calculated the interaction energy of a hydroxyl-phlogopite layer with a layer containing only the additional charges by the Madelung method (Hartman 1973). This energy is $-18.4 \text{ kJ mol}^{-1}$. Giese finds -21.7 and $-24.3 \text{ kJ mol}^{-1}$; it is not clear why his values are larger than ours. The decrease in energy was found to be mainly due to the interaction energy of the nearest hydroxyl layer with the underlying layer (9.2 kJ mol^{-1}), the next contribution being from the K^+ ion (8.5 kJ mol^{-1}), while the $\text{T}^{3.75+}$ and O^{2-} ions nearest to the surface almost cancel their contributions (-0.3 kJ mol^{-1}).

(b) The surface energies of the K^+ -containing micas are almost the same (220 kJ mol^{-1}) irrespective of whether they are di- or tri-octahedral. This is at variance with Giese's results who found clearly a higher surface energy for the 2M_1 muscovite than for the phlogopite. In order to test whether this is due to the 2M_1 polytype we calculated in a similar way as above the difference in surface energy of a di- and tri-octahedral mica. Starting from fluorphlogopite we put a charge of -2 on the Mg in the octahedron that is empty in the dioctahedral mica, and a charge of $+1$ on the other two Mg ions. Then we calculated the interaction energy of a fluorphlogopite layer with a layer consisting of the rows of the additional charges. This energy is $+0.01 \text{ kJ mol}^{-1}$, much smaller than the value of more than 20 kJ mol^{-1} found by Giese. It seems to be likely that the different layer stacking in the 2M_1 polytype could be responsible for this difference because, as pointed out by Appelo (1978), the relative stability of the 1M and 2M_1 polytypes can be related to the rotation of the octahedra involving a tilting of the tetrahedra. Appelo (1978) calculated the energy difference to be of the order of 1 kJ mol^{-1} , which leaves the 20 kJ mol^{-1} difference found by Giese unexplained.

(c) The surface energies of the micas without an interlayer cation are the same, which, in view of the above discussion, is not surprising. The negative values are probably due to the fact that hypothetical structures are used. For the true structures we may expect small positive values. The value for illite, 174 kJ mol^{-1} , is based on $x = 0.9$. Because for the surface energy the interaction between the potassium ions makes the largest contribution, this energy can be estimated to $(-7 + 0.81 \times 227) = 177 \text{ kJ mol}^{-1}$. This shows that the surface energy is roughly proportional to x^2 .

(e) *Predictions made for silicates whose full crystal structures are not determined*

(i) *Saponite*, $\text{Na}_x\text{Mg}_3(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_2$ and *fluorsaponite*, $\text{Na}_x\text{Mg}_3(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}\text{F}_2$

Saponite and its fluorine derivative are normally found as expanded micas, although their crystal structure has not been determined. The shrinkage properties of saponite on heating have

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been studied by Keifer (1957). The lattice energy of saponite is given by equation (11) which reduces under the substitution

$$q_{O'} = -1 - q_H \quad (56)$$

to the equation

$$U_{\text{elec}}(\text{'collapsed' saponite, Na}_x\text{Mg}_3(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_2) \\ = 72805 - 3735x + 299x^2 - 8xq_H + 2756q_H + 2774q_H^2 \text{ kJ mol}^{-1} \quad (57)$$

This equation simulates the silicates in table 22 under the listed substitutions, whereupon

$$U_{\text{elec}}(\text{'collapsed' saponite}) = 78335 - 3743x + 299x^2, \quad (58)$$

$$U_{\text{elec}}(\text{'collapsed' fluorsaponite}) = 72805 - 3735x + 299x^2. \quad (59)$$

TABLE 22. SILICATES OBTAINED BY APPROPRIATE x AND q_H SUBSTITUTIONS IN EQUATION (57)

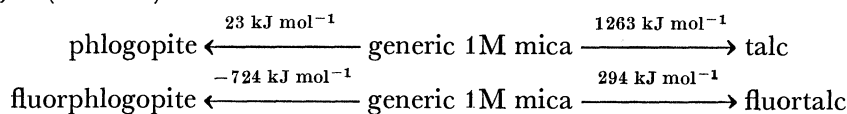
q_H	x	phyllosilicate
0.0	0.0	fluortalc
0.0	x	fluorsaponite
0.0	1.0	fluorphlogopite†
1.0	0.0	talc
1.0	x	saponite
1.0	1.0	phlogopite†

† Accepting that Na^+ is equivalent electrostatically to K^+ .

Figure 1 shows the variation of the lattice energy of saponite and fluorsaponite with x , the fraction of interlayer cation. It is interesting to find that the substitutional energy of OH for fluorine is almost independent of x and moreover is entirely consistent with the U_{subs} value of table 10.

We may speculate, leaving aside the fact that saponite is actually an expanded structure, as to how much the theoretical lattice energies of equations (51) and (52) differ from the actual lattice energies or, specifically, from the magnitude of the relaxation energy from the generic 1M mica and 1M fluormica to the saponite and fluorsaponite. We have details of U_{relax} for the extremes, talc, phlogopite, fluortalc and fluorphlogopite. Since saponite is a trioctahedral mica we may safely assume that the hydroxyl group is perpendicular to the layer.

The energies (table 13)



indicate that the dotted lines on figure 1 may offer a closer approximation to the true lattice energy variation. It is noteworthy that, once again, OH \rightarrow F substitutional energies are almost constant with respect to x variation. For 'expanded' (20 Å) saponite we can use an equation of the form of equation (11), taking into account that in the expanded structures the charges on the potassium ions are halved, so that:

$$U_{\text{elec}}(\text{'expanded' saponite, (Na}_2\text{)}_{\frac{1}{2}x}\text{Mg}_3(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_2) \\ = \sum_{i=0}^2 \sum_{j=0}^{(2-i)} \sum_{k=0}^{(2-j)} \sum_{l=0}^{(2-k)} \sum_{m=0}^{(2-l)} \sum_{n=0}^{(2-m)} \sum_{p=0}^{(2-n)} (-1)^m 2^{(m+j+k)} (0.5x)^i (4 - 0.25x)^l A_{ijklmnp} q_{O'}^n q_H^p \\ = 72812 - 3695x + 31x^2 - 7xq_H + 2757q_H + 2774q_H^2. \quad (60)$$

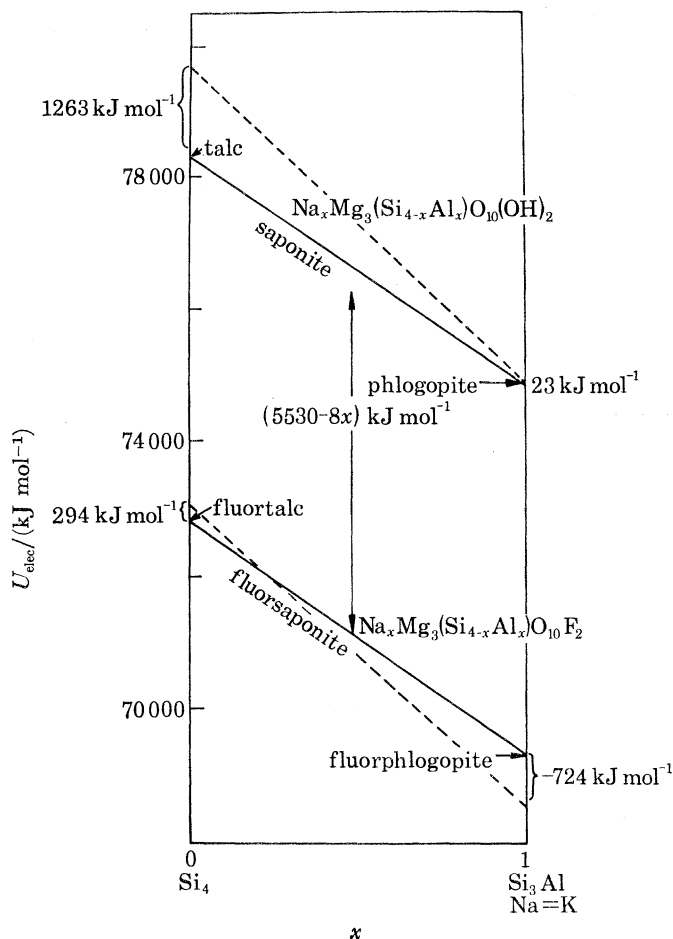


FIGURE 1. Variation of lattice energy of saponite and fluorphlogopite and parameter x .

The surface energy is obtained by subtracting equation (60) from (57) which gives:

$$\Delta U_{\text{saponite}} = -7 - 40x + 268x^2 - xq_{\text{H}} - q_{\text{H}}. \quad (61)$$

This shows the negligible influence of the $\text{F} \rightarrow \text{OH}$ substitution and the quadratic dependence on x mentioned in the foregoing section. There is a minimum of about -9 kJ mol^{-1} for $x \approx 0.075$.

(ii) *The beidellite–illite series, $\text{A}_x\text{Al}_2(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_2$ and the fluoranalogues*

For small values of x , about 0.1, and $\text{A} = \text{Na}$, the mineral is called beidellite. It is found in an expanded form. An accurate determination of its structure has not been made.

For x closer to 1 (about 0.9) and $\text{A} = \text{K}$, the mineral is called illite. The general structure characteristics were described by Grim, *et al.* (1937). The polytype considered here is, of course, the 1M illite. The lattice energy is given by equation (8):

$$\begin{aligned} U_{\text{elec}}(\text{beidellite–illite}, \text{A}_x\text{Al}_2(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_2) \\ = 76066 - 3727x + 299x^2 - 8xq_{\text{H}} + 3951q_{\text{H}} + 2774q_{\text{H}}^2. \end{aligned} \quad (62)$$

The limiting substitutions in the general formula are given in table 23.

Figure 2 gives a plot of the lattice energy (62) as a function of x in order to interpolate a true lattice energy for ‘collapsed’ beidellite.

TABLE 23. SILICATES OBTAINED BY APPROPRIATE x AND q_H SUBSTITUTION IN EQUATION (62)

q_H	x	silicate
0	0	fluorpyrophyllite
0	0.1	fluorbeidellite
0	0.9	fluorillite
0	1	1M Al fluormica
1	0	pyrophyllite
1	0.1	beidellite
1	0.9	illite
1	1	1M Al mica

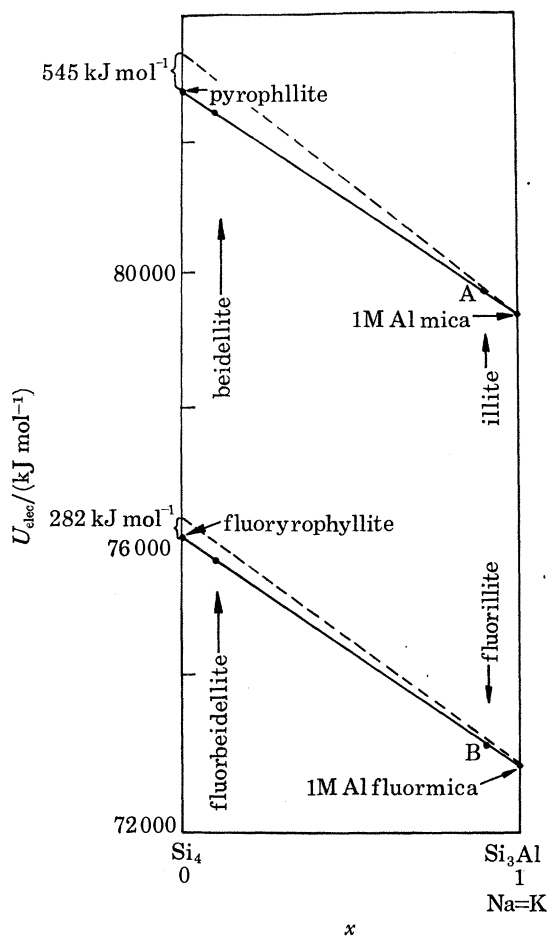
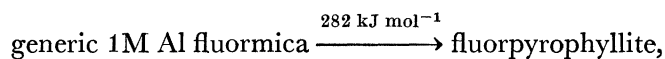
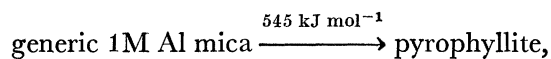


FIGURE 2. Plot of the lattice energy of beidellite mineral.

We can estimate from the relaxation energies (table 15):



the likely true lattice energies of the collapsed beidellite and fluorbeidellite. Since we know the relaxation energies at $x = 1$ are zero (since it corresponds to the generic 1M mica) and at $x = 0$

(pyrophyllites) we can estimate the variation in true lattice energy with x and obtain the corrected lattice energies:

$$U_{\text{elec}}(\text{'collapsed' beidellite}) \approx 82925 \text{ kJ mol}^{-1}, \quad (63)$$

$$U_{\text{elec}}(\text{'collapsed' fluorbeidellite}) \approx 76000 \text{ kJ mol}^{-1}. \quad (64)$$

The substitutional energy of $\text{OH} \rightarrow \text{F}$ is 6724 kJ mol^{-1} , in agreement with the dioctahedral prediction of table 10.

For illite, when $q_{\text{H}} = 0$, the lattice energy corresponds to point B for fluorillite on figure 2 while, when $q_{\text{H}} = 1$, the lattice energy corresponds to point A for illite. The relaxation correction applied leads to true energies which are very close to those calculated directly from the generic adiabatic substitution method (since the structure of illite is close to that of 1M Al mica):

$$U_{\text{elec}}(\text{illite}) \approx 79680 \text{ kJ mol}^{-1}, \quad (65)$$

$$U_{\text{elec}}(\text{fluorillite}) \approx 73050 \text{ kJ mol}^{-1}. \quad (66)$$

The substitutional energy of $\text{OH} \rightarrow \text{F}$, 6718 kJ mol^{-1} , is maintained in line with table 10.

For the 'expanded' beidellite derived from the expanded 20 \AA generic mica we find

$$\begin{aligned} U_{\text{elec}}(\text{'expanded' beidellite}, (\text{Na}_2)_{\frac{1}{2}x} \text{Al}_2(\text{Si}_{4-x}\text{Al}_x)\text{O}_{10}(\text{OH})_2) \\ = 76073 - 3688x + 31x^2 - 7xq_{\text{H}} + 3952q_{\text{H}} + 2774q_{\text{H}}^2. \end{aligned} \quad (67)$$

This equation also holds for the expanded illite. The surface energy is obtained by subtracting equation (67) from (62):

$$\Delta U_{\text{elec}}(\text{beidellite} - \text{illite}) = -7 - 39x + 268x^2 - xq_{\text{H}} - q_{\text{H}}. \quad (68)$$

This equation is almost the same as that derived for saponite, a trioctahedral mica. For beidellite, with $x = 0.1$, a surface energy of -8 kJ mol^{-1} is obtained while for illite with $x = 0.9$ the surface energy is about 174 kJ mol^{-1} . In all the limiting minerals, the OH groups are not perpendicular to the interlayer, and so we may safely assume that the same holds for the beidellite–illite series.

(iii) *Montmorillonite*, $\text{Na}_x\text{Al}_{2-x}\text{Mg}_x\text{Si}_4\text{O}_{10}(\text{OH})_2$, and *fluormontmorillonite* $\text{Na}_x\text{Al}_{2-x}\text{Mg}_x\text{Si}_4\text{O}_{10}\text{F}_2$

The montmorillonite minerals occur in extremely small particles so that single crystal X-ray diffraction data cannot be obtained. Any structural concepts must be deduced from X-ray powder data or from electron diffraction studies on single crystals. Hofmann *et al.* (1933), Marshall (1935), Maegdefrau & Hofmann (1937) and Hendricks (1942) have all contributed ideas as to the structural features. Equation (15) gives the lattice energy of 'collapsed' montmorillonite; it takes the form

$$\begin{aligned} U_{\text{elec}}(\text{'collapsed' montmorillonite}, \text{Na}_x\text{Al}_{2-x}\text{Mg}_x\text{Si}_4\text{O}_{10}(\text{OH})_2) \\ = 76066 - 2009x + 20x^2 - 284xq_{\text{H}} + 3951q_{\text{H}} + 2774q_{\text{H}}^2. \end{aligned} \quad (69)$$

When $x = 1$ and $q_{\text{H}} = 1$ we have the mineral leucophyllite, $\text{KAlMgSi}_4\text{O}_{10}(\text{OH})_2$, for which

$$U_{\text{elec}}(\text{leucophyllite}, \text{KAlMgSi}_4\text{O}_{10}(\text{OH})_2) = 80518 \text{ kJ mol}^{-1}, \quad (70)$$

and when $q_{\text{H}} = 0$,

$$U_{\text{elec}}(\text{fluorleucophyllite}, \text{KAlMgSi}_4\text{O}_{10}\text{F}_2) = 74077 \text{ kJ mol}^{-1}. \quad (71)$$

For montmorillonite-type minerals, the substitutional energy of $\text{OH} \rightarrow \text{F}$ is $(6725 - 284x) \text{ kJ mol}^{-1}$,

DIOCTAHEDRAL AND TRIOCTAHEDRAL PHYLLOSILICATES 203

having a greater dependence on x than we have seen in the other minerals. This is understandable in that when $x = 1$ we have the mineral $\text{KAlMgSi}_4\text{O}_{10}(\text{OH})_2$, and when $x = 0$ we have $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$, pyrophyllite. In the case of leucophyllite, $x = 1$ and the substitutional energy of $\text{OH} \rightarrow \text{F}$ is 6441 kJ mol^{-1} ; this differs from the entries in table 10 because the dioctahedral sites in this dioctahedral silicate are occupied by an Al and a Mg atom. The normal $\text{OH} \rightarrow \text{F}$ substitutional energy (table 10) for a dioctahedral mica is 6721 kJ mol^{-1} , the difference of -284 kJ mol^{-1} representing the energy of exchanging a Mg atom in the dioctahedral site. Figure 3 shows a graph of the variation of the lattice energy of montmorillonite with x .

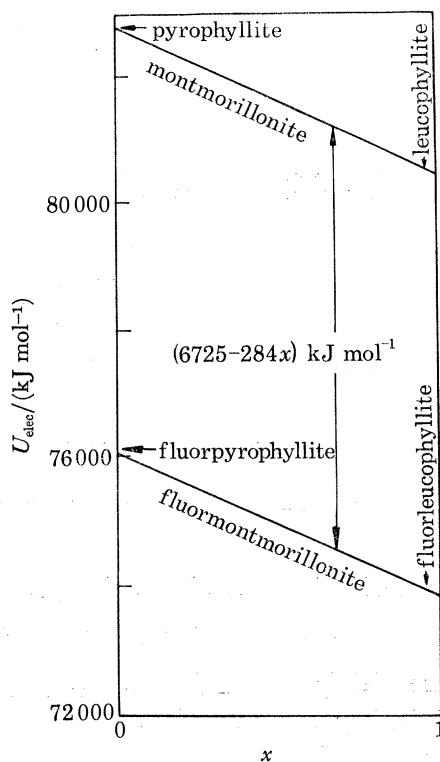


FIGURE 3. Variation of lattice energy of montmorillonite and fluormontmorillonite with parameter x .

The relaxation correction that has been applied to the minerals treated in the above sections cannot be estimated for figure 3, since we are only able to apply it for pyrophyllite and fluorpyrophyllite and have no means of estimation for leucophyllite.

For 'expanded' montmorillonite, as derived from the generic 20 \AA mica, we find

$$U_{\text{elec}}(\text{'expanded' montmorillonite, } (\text{Na}_2)_{\frac{1}{2}x}\text{Al}_{2-x}\text{Mg}_x\text{Si}_4\text{O}_{10}(\text{OH})_2) \\ = 76073 - 1973x - 262x^2 - 283xq_{\text{H}} + 3952q_{\text{H}} + 2774q_{\text{H}}^2. \quad (72)$$

The surface energy is found as the difference between equations (68) and (61).

$$\Delta U_{\text{elec}}(\text{montmorillonite}) = -7 - 36x + 282x^2 - xq_{\text{H}} - q_{\text{H}}. \quad (73)$$

This gives a surface energy of 239 kJ mol^{-1} for fluorleucophyllite and 237 kJ mol^{-1} for leucophyllite. We see that the substitution in the octahedral layer increases the surface energy with respect to substitution in the tetrahedral layer by about 18 kJ mol^{-1} when $x = 1$.

It is interesting to consider the difference in lattice energy between the minerals of the beidellite–illite series with substitution in the tetrahedra on the one hand and the montmorillonite, with substitution in the octahedra on the other

$$U_{\text{elec}}(\text{'collapsed' montmorillonite}) - U_{\text{elec}}(\text{'collapsed' beidellite–illite}) = 7 + 1718x - 279x^2 - 276xq_{\text{H}}. \quad (74)$$

The result shows that, at least for the unrelaxed structures, the montmorillonite would be the more stable one according to electrostatic arguments. For small x , no data are known and usually the minerals montmorillonite and beidellite are not distinguished by the routine X-ray identification. For $x \approx 1$, this is at variance with the fact that leucophyllite is a rare mineral, while illite is one of the most important ones. This shows that the relaxation energies should not be neglected.

(iv) *Collapsed hectorite*, $\text{Na}_x\text{Mg}_{(2-x+xy)}\text{Li}_{(1-y)x}\text{Mg}_{(1-xy)}\text{Li}_{xy}\text{Si}_4\text{O}_{10}(\text{OH})_2$

and *fluorhectorite*, $\text{Na}_x\text{Mg}_{(2-x+xy)}\text{Li}_{(1-y)x}\text{Mg}_{(1-xy)}\text{Li}_{xy}\text{Si}_4\text{O}_{10}\text{F}_2$

The lattice energy is given by equation (12) for the mineral having Mg and Li at both the di- and trioctahedral sites while equation (13) gives the lattice energy when the Li atoms are solely at the X' sites, and equation (14) gives the lattice energy when Li atoms reside solely at the X sites. Hence, in general,

$$U_{\text{elec}}(\text{'collapsed' hectorite}, \text{Na}_x\text{Mg}_{(2-x+xy)}\text{Li}_{(1-y)x}\text{Mg}_{(1-xy)}\text{Li}_{xy}\text{Si}_4\text{O}_{10}(\text{OH})_2) = 72805 - 1293x + 20x^2 - 358x^2y - 284xq_{\text{H}} + 538x^2y^2 + 555xy + 2756q_{\text{H}} + 597xyq_{\text{H}} + 2774q_{\text{H}}^2, \quad (75)$$

and

$$U_{\text{elec}}(\text{'collapsed' fluorhectorite}, \text{Na}_x\text{Mg}_{(2-x+xy)}\text{Li}_{(1-y)x}\text{Mg}_{(1-xy)}\text{Li}_{xy}\text{Si}_4\text{O}_{10}\text{F}_2) = 72805 - 1293x + 20x^2 - 358x^2y + 538x^2y^2 + 555xy. \quad (76)$$

When $x = 1$, we have the structure $\text{NaMg}_{(1+y)}\text{Li}_{(1-y)}\text{Mg}_{(1-y)}\text{Li}_y\text{Si}_4\text{O}_{10}(\text{OH})_2$: for $y = 1$ the Li atoms at the X site disappear and the Mg atom at the X' site disappears, thus leaving Li solely at X' and Mg solely at X ($\text{NaMg}_2\text{LiSi}_4\text{O}_{10}(\text{OH})_2$). In the case where $y = 0$, we have MgLi at the X site and Mg at the X' site. The general equation for $x = 1$ is

$$U_{\text{elec}}(\text{NaMg}_{(1+y)}\text{Li}_{(1-y)}\text{Mg}_{(1-y)}\text{Li}_y\text{Si}_4\text{O}_{10}(\text{OH})_2) = 71532 + 197y + 538y^2 + 2472q_{\text{H}} + 597yq_{\text{H}} + 2774q_{\text{H}}^2. \quad (77)$$

When $x = 0$ and $y = 0$, we have the structure $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ (talc) and equation (75) reduces to

$$U_{\text{elec}}(\text{talc}) = 72805 + 2756q_{\text{H}} + 2774q_{\text{H}}^2, \quad (78)$$

which is the form taken by equation (4).

Equation (77) when $y = 0$ gives for $q_{\text{H}} = 1$,

$$U_{\text{elec}}(\text{NaMgLiMgSi}_4\text{O}_{10}(\text{OH})_2) = 76778 \text{ kJ mol}^{-1}, \quad (79)$$

and, when $q_{\text{H}} = 0$,

$$U_{\text{elec}}(\text{NaMgLiMgSi}_4\text{O}_{10}\text{F}_2) = 71532 \text{ kJ mol}^{-1}. \quad (80)$$

When $y = 1$ and $q_{\text{H}} = 1$,

$$U_{\text{elec}}(\text{NaMg}_2\text{LiSi}_4\text{O}_{10}(\text{OH})_2) = 78110 \text{ kJ mol}^{-1}, \quad (81)$$

and when $y = 1$ and $q_H = 0$,

$$U_{\text{elec}}(\text{NaMg}_2\text{LiSi}_4\text{O}_{10}\text{F}_2) = 72267 \text{ kJ mol}^{-1}. \quad (82)$$

These results are plotted in figure 4.

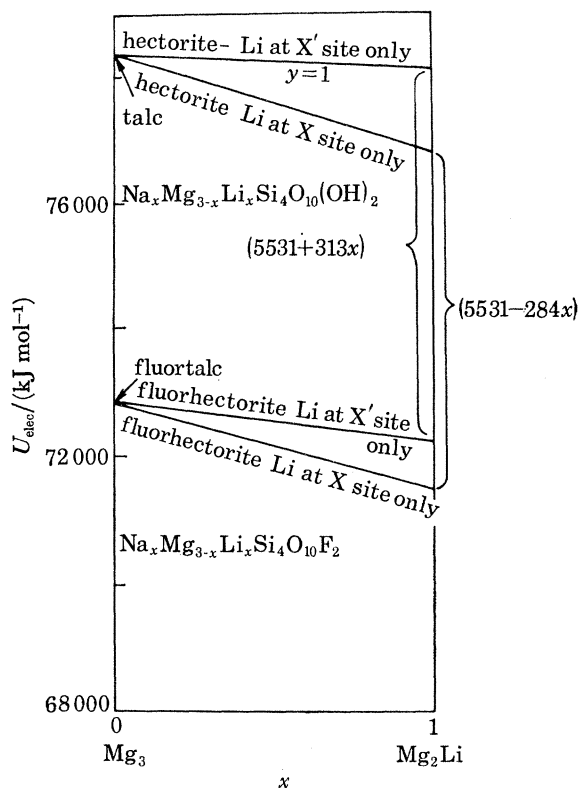
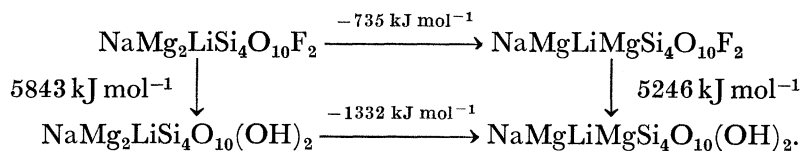


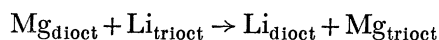
FIGURE 4. Variation of lattice energy of hectorite and fluorhectorite with x and y .

From such results we find



Since the structures are all derived from the generic 1M mica, the above energies represent substitutional energies. The $\text{F} \rightarrow \text{OH}$ energy, 5843 kJ mol^{-1} , is of similar order to that expected for a trioctahedral mica (316 kJ mol^{-1} higher, see table 10). In the other case the $\text{F} \rightarrow \text{OH}$ substitutional energy amounts to 5246 kJ mol^{-1} (287 kJ mol^{-1} lower than expected) and the differences (*ca.* 5%) arise from the fact that Na and Li are present as modifying ions.

The energy for the substitutional changes



amounts to -735 kJ mol^{-1} , and it is clear that the silicates having Mg solely at the dioctahedral site and Li solely at the additional trioctahedral site are more stable than those having a Mg at both di- and trioctahedral sites with a Li at the dioctahedral site. The difference between the 'adiabatic' generically derived energy for hectorites where x is small is probably of the order of

1250 kJ mol⁻¹ for the hydroxy silicates and only of the order of about 300 kJ mol⁻¹ for the fluorinated silicates (cf. 1M mica and talc).

The corresponding equations for the 'expanded' hectorites based on the 20 Å generic 1M mica structure are

$$U_{\text{elec}}(\text{'expanded' hectorite, } (\text{Na}_2)_{\frac{1}{2}x}\text{Mg}_{(2-x+xy)}\text{Li}_{(1-y)x}\text{Mg}_{(1-xy)}\text{Li}_{xy}\text{Si}_4\text{O}_{10}(\text{OH})_2) \\ = 72812 - 1257x - 262x^2 - 358x^2y - 283xq_{\text{H}} + 538x^2y^2 + 555xy + 2757q_{\text{H}} + 2774q_{\text{H}}^2. \quad (83)$$

The surface energy is found as the difference between equations (75) and (83)

$$\Delta U_{\text{elec}}(\text{hectorite}) = -7 - 37x + 282x^2 - xq_{\text{H}} - q_{\text{H}}. \quad (84)$$

This surface energy is independent of y , that is, independent of the site at which Li is concentrated. This is in agreement with the fact that we find virtually no difference between the surface energies of di- and trioctahedral micas. For $x = 1$, we obtain the hypothetical mineral NaMg₂LiSi₄O₁₀(OH)₂ and the fluor-analogue, which has on average a surface energy of 237 kJ mol⁻¹, which is almost the same as for the leucophyllites where the substitutions take place solely in the octahedral layer.

6. CONCLUSIONS

The approach presented in this paper is new and from a matter of only seven computer calculations we are able to discuss the energetics of a wealth of silicate minerals, to comment on substitutional and relaxation energies from an electrostatic viewpoint, and also to predict the correction term in order to establish true electrostatic lattice energies from those calculated from imprecise structures. The calculations derived from a generic structure are shown to be, at most, about 1.6 % in error when compared with the individual calculations based on the true silicate structure, and in most cases the error is a good deal smaller. The subterfuge of considering substitutional changes without the accompanying relaxation changes extends the predictive powers of the calculations, as well as saving dramatically the computer time necessary. Among a number of points that emerge from these electrostatic calculations is the apparent quadratic dependence of the surface energies on x in the minerals derived from $\text{K}_x\text{X}_2\text{X}'\text{T}_4\text{O}_{10}(\text{OH})_2$.

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APPENDIX 1. CORRECTION OF THE SURFACE ENERGY FOR AN ORDERED ARRANGEMENT OF THE INTERLAYER CATION

The lattice energies of the expanded structures are based on layers bounded on either side by K^+ ions having a charge $\frac{1}{2}q_K$. To obtain the surface energy for an ordered arrangement of the K^+ ions, we superimpose a layer of charges $+\frac{1}{2}q_K$ on the K^+ ions at the sites $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 1)$ and a layer of charges $-\frac{1}{2}q_K$ on the K^+ ions at the sites $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(0, 0, 1)$. The result is that we have rows of K^+ ions with charges q_K in the direction of the a axis and going through the sites $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 1)$, while similar rows through $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(0, 0, 1)$ are now empty. The stacking of these slices upon one another in the non-expanded structure will again produce the normal crystal structure.

The change in electrostatic energy of the slice contains two parts: the interaction energy of the added charges with (i) each other and (ii) all other ions that were present before. This second interaction energy is zero since the K^+ ions at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ are identical by translation, so that at these sites the potentials are equal and the energies cancel because the added ions have opposite charges. The same holds for the sites $(0, 0, 1)$ and $(\frac{1}{2}, \frac{1}{2}, 1)$. Thus we are left with the interaction energy of the added charges among themselves. This has been calculated by the Madelung method outlined by Hartman (1973) and gave the value 92.3 kJ mol^{-1} for the true structure of fluorphlogopite. Since the lattice energy is not altered, the surface energy, or better the term E_1 , is lowered by the same amount. The term E_1 has also been calculated by the Madelung method for the case where all potassium ions have a charge $+\frac{1}{2}$. The details of this calculation will be published elsewhere (Hartman 1979), but the result was 201 kJ mol^{-1} , from which we find a corrected surface energy of 109 kJ mol^{-1} which is to be compared to the value $113.8 \text{ kJ mol}^{-1}$ obtained by Giese and based on the same coordinates.

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