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ORIGINAL PAPER

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Effect of the Si/Al ordering on structural parameters and the energetic stabilization of vermiculites – a theoretical study

Abstract The effect of the Si/Al distribution in the tetrahedral sheets of the vermiculite mineral has been investigated employing density functional theory. The structures of six models for vermiculite with the structural formula $(Mg_4)(Mg_{12})(Si_8Al_8)O_{40}(OH)_8 \cdot 24(H_2O)$ per unit cell were fully optimized. The models differ by the $T \cdots Mg^{2+} \cdots T'$ coordination of the interlayer Mg^{2+} cations by two central cations from the adjacent tetrahedral sheets of the 2:1 vermiculite layers (T,T' = Si,Al). We observed the formation of very strong hydrogen bonds between water molecules solvating the interlayer Mg^{2+} cations and the surface basal oxygen atoms of the 2:1 layers. The directionality of hydrogen bonds is the major factor determining the layer stacking in the vermiculite structure. Results showed that the most stable model is that where only silicon atoms in the tetrahedral sheets coordinate all interlayer Mg^{2+} cations.

Keywords Vermiculite · Density functional theory · Calculation

Introduction

Vermiculites are expandable 2:1 clay minerals formed in soils from the weathering of micas and chlorites (Shulze 1989). Their 2:1-layer structure consists of two tetrahedral sheets bound to either side of an octahedral sheet via the plane of basal oxygen atoms (see Fig. 1). The outer two planes of the layer are formed from the basal oxygen atoms. The structure of vermiculite layers can be derived from the structure of the layers of the simplest 2:1 phyllosilicates—talc and pyrophyllite. Talc has Mg^{2+} cations in all possible octahedral sites and is of a trioctahedral type while pyrophyllite has only 2/3 of the octahedral sites occupied by Al^{3+} cations and is of the dioctahedral type. Tetrahedral sheets in both minerals contain only Si^{4+} cations. In both cases layers are electrically neutral and held together only by weak dispersion forces between layers. The 2:1-layer structure of vermiculite minerals differs from talc and pyrophyllite mainly in the chemical composition. A part of tetrahedral sites is occupied by trivalent cations (e.g. Al^{3+}, Fe^{3+}) instead of Si^{4+} (in some cases also isomorphic substitution in the octahedral sheet can occur). This substitution results in an excess of the negative charge per formula unit, which is compensated by cations in the interlayer space, similar to the situation occurring in micas. While in micas the charge per formula is about −1 or more and mainly K^+, Na^+ and Ca^{2+} are compensating cations, in vermiculites the charge is lower (from -0.6 to −0.9) and compensating cations are hydrated Mg^{2+} and Ca^{2+} in most cases. However, in some cases vermiculite structures have excess charge larger than −1.5 (Van Olphen 1969). Forces keeping layers in vermiculites together are of Coulombic nature supported by strong hydrogen bonds. In contrast to micas, the interlayer counter ions are exchangeable and can be replaced by various monovalent or divalent cations (e.g. Li^+, Na^+, K^+, Cs^+, NH_4^+, Ni^{2+}). The amount of interlayer water in vermiculites is variable and depends on physicochemical conditions. The interlayer spacing, d, depends on this confined interlayer water (Smalley 1994).

The structures of natural Mg-vermiculites are known from the pioneering investigations of Hendricks and Jefferson (1938), Mathieson and Walker (1954) and Shirozu and Bailey (1966). Later experimental work was focused on different cation–water complexes, layer-stacking orders and the structure of interlayer water. A summary of these aspects is given in the review of de la Calle and Suquet (1988). Interlayer structures of the two-layer hydrates of Na- and Ca-vermiculites were

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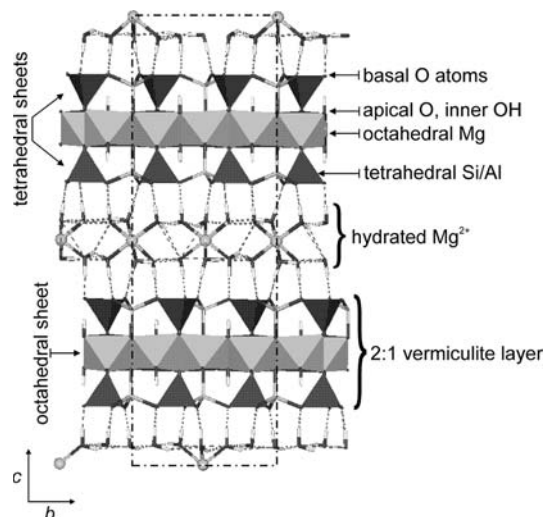1090 Vienna, Austria

Fig. 1 The structure of *2M* vermiculite. The unit cell drawn as dash-dot line

studied by X-ray diffraction (Slade et al. 1985). Neutron diffraction was used in the study of Ca- and Li-vermiculites (Skipper et al. 1994, 1995). Structure and dynamics of water layers in various vermiculites were also studied (Skipper et al. 1991; Swenson et al. 2000, 2001, 2002). The effect of dehydration and rehydration on the structural order was observed for several natural vermiculites (von Reichenbach and Beyer 1994, 1997; Beyer and von Reichenbach 1998, 2002).

In spite of the intensive experimental studies of vermiculites several problems are still open: for example, how cation substitution in the tetrahedral sheet affects hydrogen bond formation and, consequently, the stacking order of vermiculite layers. Computer simulations can give new and deeper insight into the mentioned problems and can help in the interpretation of experimental results. Several investigations have been published where an ab initio approach applying periodic boundary conditions has been used in the study of clay minerals using either real structures or simplified models (Hess and Saunders 1992; Bridgeman et al. 1996; Odelius et al. 1997, Balan et al. 2001; Benco et al. 2001a,b,c, Stackhouse et al. 2001; Teppen et al. 2002; Tunega 2002). Calculations employing empirical interatomic potentials are applied in studies of more complicated mineral systems because of the significantly reduced computational effort as compared to the aforementioned ab initio methods. As examples we want to mention Monte Carlo simulation studies on the cation ordering in the muscovite mineral (Palin et al. 2001) and in illites and smectites (Saint-Diaz et al. 2001).

The aim of the present ab initio study is to investigate structural features and the energetic stabilization of vermiculite models with respect to the T···Mg···T′ coordination where T/T′ are Si or Al atoms from the tetrahedral sheets neighbouring the interlayer Mg^{2+} cation. In this arrangement the distribution of the tetrahedral

substitutions extends along the *c* direction. Experimentally, this information is not easily accessible, but it is important for the interlayer ordering of the counter ions. Additionally, the positions of H atoms and the interlayer H_2O orientation can be computed very accurately, applying an ab initio approach. Of further great interest is the hydrogen-bond formation between vermiculite layers and hydrated interlayer cations and the effect of these hydrogen bonds on the layer stacking. Especially the accurate description of the hydrogen-bond formation is very important since simulation methods using classical empirical potentials often fail in this respect due to inadequate potential parameters. Moreover, the difficulties in locating H atoms by standard X-ray diffractions methods are well known.

Structural and computational details

Structural details

The structure of the natural Mg-vermiculite mineral from the Llano locality in Texas served as the basis for our structural models. The experimental structure was derived by Shirozu and Bailey (1996) using X-ray diffraction and belongs to the *2M* vermiculite polytype possessing the C2/c space group. The unit-cell parameters obtained in that work are as follows: $a = 5.349(6)$, $b = 9.255(10)$, $c = 28.89(2)$ Å and $\beta = 97.12(10)°$. Corresponding chemical analytical formula is:

$$(Mg0.48K_{0.1})(Mg_{2.83}Fe_{0.01}Al_{0.15})$$
$$(Si_{2.86}Al_{1.14})O_{10}(OH)_2 \cdot 4.72(H_2O).$$
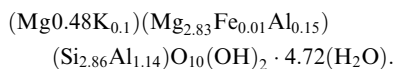
The atoms in the first parentheses represent cations in the interlayer space, the second contain cations in the octahedral sheets and the third represent central cations in the tetrahedral sheets. One can see from the formula that the major substitution occurs in the tetrahedral sheet (Si by Al) but that also minor substitution is taking place in the octahedral sheet (Mg/Fe,Al). Certain negligible impurities were also detected (K, Fe). For the purpose of our ab initio simulations a simplified model had to be developed. Neglecting minor substitutions and impurities, conserving the total charge zero of the unit cell and applying the symmetry operations, we arrived at a supercell with the composition $(Mg_2)(Mg_{12})(Si_{12}Al_4)O_{40}(OH)_8 \cdot 24(H_2O)$. This means that each fourth silicon atom in the tetrahedral sheet is replaced by an aluminium atom. Each substitution results in the charge −1, which is compensated formally by one half of the charge of the Mg^{2+} cation. The cell obtained in this way served as the computational unit cell. Since we wanted to study the effect of the distribution of the Si/Al substitution in the tetrahedral sheets, we did not consider any symmetry operation inside the unit cell. Therefore, the space group of the computational unit cell is always P1. The Si/Al ratio 3/1 gives two aluminium atoms in one 2:1 vermiculite layer leading to 16 combinations. Taking into the account that two layers are in the unit cell of the *2M* vermiculite, the number of possible structural configurations increases to 256. Thus, in order to reduce the structural manifold, we performed the following steps. Additional substitution of one Si by Al in the tetrahedral sheet was performed. This means that each second atom in the tetrahedral sheet is aluminium. In the case of such half substitution, the Löwenstein rule implies a regular alternate Si/Al substitution pattern in the tetrahedral sheet. This additional substitution results in an increase of the negative charge per formula unit to −2, requiring additional compensation by adding another Mg^{2+} cation into the interlayer space. Such high negative excess charge is more typical for mica structures. However, Van Olphen (1969) published also experimental data for the vermiculite structure with the layer charge of −1.6.

For the interlayer cations compensating the negative charge of the layer at least two distinct places are considered. One place is above the ditrigonal hole of the bottom layer and below the triangle formed from the basal oxygen atoms of the upper layer. The second possibility is above and below the triangle formed from the basal oxygen atoms connected to the same central tetrahedral cation. Experiments with divalent cations in the interlayer space of vermiculites showed that the preferred position is the second one (Shirozu and Bailey 1966; Slade et al. 1985; von Reichenbach and Beyer 1994, 1997; Beyer and von Reichenbach 1998). In the case of the Si/Al substitution of 3/1 only half of them is occupied. Thus, in our case of 2/2 substitution the required additional compensating Mg^{2+} cation went naturally to the free site above and below the basal oxygen triangle also. The second important feature of the vermiculite structures is the variable amount of water in the interlayer space. It is known that the coordination of divalent cations is usually six. In the structural work of Shirozu and Bailey (1966) such coordination of the Mg^{2+} was suggested also. Therefore, in our work we considered only sixfold coordination of the Mg^{2+} cation by water molecules and no additional free water molecules in the interlayer space. In such an arrangement any water molecules shared by two adjacent Mg^{2+} cations do not occur.

Summarizing, our vermiculite model contains two Mg^{2+} cations in one interlayer space in the cell, each one coordinated by six water molecules. Each vermiculite layer has four Si/Al substitutions. The full structural formula of our model per computational cell is $(Mg_4)(Mg_{12})(Si_8Al_8)O_{40}(OH)_8 \cdot 24(H_2O)$. For a structural characterization of this model see Fig. 1. Since we have two vermiculite layers in the cell, the amount of possible configurations is still large. Six characteristic configurations, which are labelled AlAlAlAl, AlSiSiSi, AlSiAlSi, SiAlAlSi, SiAlAlAl and SiSiSiSi, were selected. These abbreviations indicate the nearest-neighbour T···Mg···T′-T″···Mg···T‴ coordination of the Mg interlayer cations in two interlayer spaces along the c direction (T, T′, T″ and T‴ are the central tetrahedral cations in two layers per unit cell). In choosing the six representatives we assumed that, for example, AlSiSiSi and the three other permutations (SiAlSiSi, SiSiAlSi, SiSiSiAl) were very similar from the energetic point of view. As illustration, the closest tetrahedra to the Mg^{2+} cations are visualized by a stick model in Fig. 1, while the tetrahedra not directly coordinated Mg^{2+} cations are presented by a dark grey tetrahedral model.

Computational details

Ab initio total-energy geometry optimizations were performed using the Vienna ab initio simulation package (VASP) (Kresse and Hafner 1993; Kresse and Furthmüller 1996) developed for periodical systems. For the exchange-correlation functional of the density functional theory, the localized density approximation (LDA) according to Perdew and Zunger (1981), together with the generalized gradient approximation (GGA) according to Perdew and Wang (1992), have been used. The calculations are performed in a plane-wave basis set using the projector-augmented wave (PAW) method (Blöchl 1994; Kresse and Joubert 1999) and ultrasoft pseudopotentials (Vanderbilt 1990; Kresse and Hafner 1994). Since the computational unit cell is sufficiently large, the Brillouin-zone sampling is restricted to the Γ point, using modest smearing of the eigenvalues to improve total energy convergence. The geometry optimizations were performed in two ways. In the first case, the experimental unit-cell parameters of Shirozu and Bailey (1966) were kept constant and all atoms were allowed to relax. Since we used relatively large variations in the structural compositions of our models, in the second step also all unit-cell parameters, together with the atomic positions, were optimized. The energy cutoff of 500 eV was used for the plane wave expansion allowing for an extended basis set and high-precision calculations. The convergence criteria were 0.00001 eV for the energy change and 0.05 eVÅ^{-1} for the rms residual force.

Results and discussion

At the beginning we want to discuss the general structural features. Bonds can be classified into three basic groups: (1) polar covalent bonds in the 2:1 layer, (2) bonds between interlayer cations and interlayer water molecules and (3) hydrogen bonds formed either between the 2:1 layers and interlayer water or between the interlayer water molecules with themselves. Only averaged values over all six models will be given in the subsequent discussion. Interatomic distances and angles are given from full optimizations including unit-cell parameters. However, it is noted that the differences to the results from restricted optimizations are practically negligible.

2:1 layer

There are two basic structural features within the individual 2:1 layer – bond distances in the octahedral sheet and bond distances in the tetrahedral sheet. In the octahedral sheet there is no substitution of the six-coordinated Mg cation. However, the cation substitution in the tetrahedral sheet significantly affects $Mg-O_a$ distances (O_a is the apical oxygen atom connecting octahedral and tetrahedral central cations). Shirozu and Bailey (1966) reported two sets of $Mg-O_a$ distances – shorter ones (2.026–2.087 Å) and longer ones (2.099–2.113 Å). The computed averaged $Mg-O_a$ distances are 2.161 Å for Si in the tetrahedral position and 2.042 Å in case of Al, which corresponds to experimental results. Thus, the $Mg-O_a$ distance can serve as an indicator for the kind of substitution in the tetrahedral sheet. Bond distances in the tetrahedral sheets differ significantly with respect to which cation is in the central position. Calculated averaged $Si-O_a$ and $Al-O_a$ distances are 1.620 and 1.712 Å, respectively. Shirozu and Bailey (1966) presented two values for $T-O_a$ distances – 1.624 and 1.682 Å. However, they were not able to identify the type of the tetrahedral cation. From our calculations this identification is clear and the calculated $T-O_a$ bond distances are in quite good agreement with the experimental values. Computed bond distances to the basal oxygen atom (O_b) are 1.663 Å for $Si-O_b$ and 1.799 Å for $Al-O_b$, which indicates a relatively large expansion of the tetrahedron containing aluminium. Similarly to the case of $T-O_a$ distances Shirozu and Bailey (1966) were not able to distinguish between $Si-O_b$ and $Al-O_b$ distances; they reported only two different, averaged $T-O_b$ values (1.647 and 1.670 Å). The difference is not as large as between calculated values, but is still significant. Shirozu and Bailey (1966) also concluded that the total averaged value of the T–O distance in the tetrahedral sheet varies with the Si/Al ratio and increases with increasing content of Al. For example, they present an average of 1.657 Å for the 3:1 ratio. In our case, we have obtained an averaged value 1.699 Å for the 2:2 ratio,

which agrees with the conclusion of Shirozu and Bailey (1966).

Interlayer region

This is the region of hydrated Mg^{2+} cations, each coordinated by 6 water molecules. Relaxed $Mg(OH_2)_6$ octahedra are slightly distorted in comparison to the ideal shape due to interactions with the 2:1 layers and with other, neighbouring $Mg(OH_2)_6$ complexes. The average Mg–O distance for the hydrated Mg^{2+} cation is 2.115 Å. This is somewhat larger than the experimental value of 2.073 Å (Shirozu and Bailey 1966).

The most interesting feature in the interlayer region is the hydrogen bond formation. We observed two types of hydrogen bonds – one type formed between water molecules and the 2:1 layer and another formed between water molecules themselves (see Fig. 2). Interlayer Mg^{2+} cations are coordinated in our model in such way that one half of coordination water molecules form one water layer and contacts the upper 2:1 layer and the second half forms another water layer contacting the bottom 2:1 layer. The water molecules in both layers are relatively ordered and their orientation is determined by the formation of hydrogen bonds. One hydrogen atom of each water molecule is oriented almost perpendicular to the (001) plane and forms very strong hydrogen bonds with the basal oxygen atoms of the 2:1 layer. The strength of the $OH{\cdots}O_b$ bonds is clearly documented by their length (average value of 1.517 Å). Moreover, these bonds are almost 100% collinear (average value of the $O_b{\cdots}H–O$ angle is 175.1°). Also, the O–H distances of the water molecules involved in these strong hydrogen bonds are significantly larger than in the free water molecule. The calculated averaged value is 1.044 Å while for the free water molecule the calculated value is of 0.985 Å (Tunega et al. 2002). These hydrogen bonds are supporting the Coulomb interactions keeping vermiculite layers together and participate in the formation of the layer stacking and the interlayer extension. In contrast to the Coulomb interactions, the hydrogen bonds display a very specific directionality. Since the three protons of the water triad coordinated to one Mg^{2+} cation contact three basal oxygen atoms connected to the same tetrahedral cation, the $T{\cdots}Mg{\cdots}T'$ moiety is practically collinear. A perpendicular view onto the (001) plane shows this fact clearly (Fig. 2). In this figure the section of the vermiculite structure between tetrahedral sheets of two adjacent 2:1 layers is illustrated. The Si(Al) and O_b atoms from the tetrahedral sheets of the upper and bottom layer are presented in dark and light grey colour, respectively. Almost perfect layer stacking of two adjacent layers is clearly seen. The $T{\cdots}Mg{\cdots}T'$ ordering is also visible in this figure and is highlighted as a semitransparent area. Aspects of energetic stabilization of this $T{\cdots}Mg{\cdots}T'$ coordination with respect to the T,T′ substitution will be discussed later.
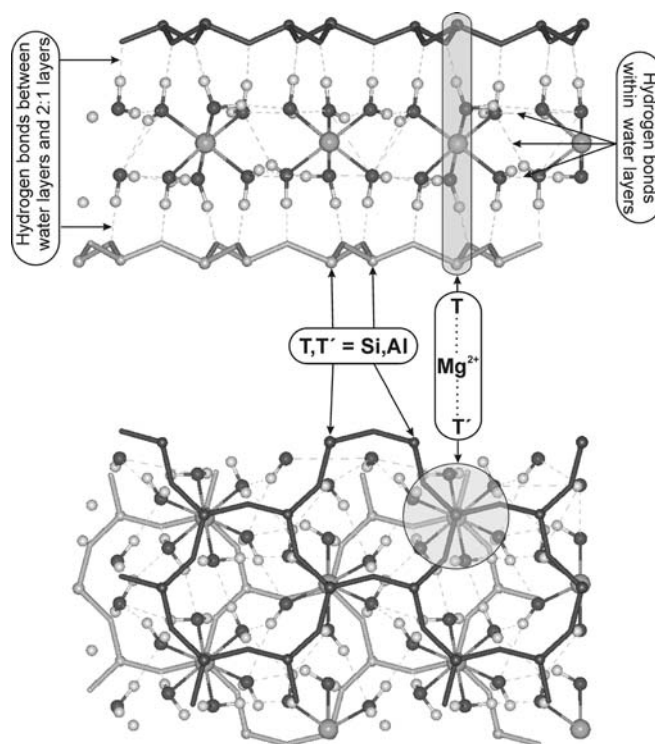

Fig. 2 Hydrogen bonds formed in the interlayer region of vermiculite

The second type of the hydrogen bonds in the interlayer region is formed between water molecules from coordination spheres of hydrated Mg^{2+} cations. Protons involved in these hydrogen bonds are located almost exactly in the plane of the water oxygen atoms (see Fig. 1). These protons contact neighbouring water oxygen atoms and a network of hydrogen bonds is formed. Hydrogen bond lengths in the interval between 1.7 and 2.4 Å are found and $O{\cdots}H–O$ angles range in the interval between 145 and 165°. Of course, these hydrogen bonds are not ideally linked as in liquid water, since the positions and orientation of water molecules in the interlayer space is strongly affected by requirements for the coordination of the interlayer cation and the formation of the strong hydrogen bonds with the 2:1 layer.

Volume relaxation

Table 1 collects result of optimized cell parameters and calculated total volumes for all six models studied. One can see that the differences of the calculated parameters to experimental values are small. The largest difference is observed for the c parameter (more than 0.2 Å compared to the experimental value). This deviation is easily understood since the c parameter is the most sensitive to the hydrogen-bond formation between vermiculite layers and the hydrated Mg^{2+} layer in the interlayer space. The computed c value is smaller than the experimental one. This has the largest effect on the fact that the

Table 1 Unit-cell parameters obtained from full relaxation for all six models studied

Model	a	b	c	α / °	β / °	γ / °	Volume Å^{-3}
AlAlAlAl	5.313	9.307	28.604	89.85	97.21	90.11	1403.249
SiAlAlAl	5.319	9.305	28.623	89.78	97.24	90.20	1405.423
SiAlSiAl	5.322	9.307	28.625	89.98	97.18	90.26	1406.638
SiAlAlSi	5.321	9.307	28.635	90.09	97.22	90.05	1406.899
AlSiSiSi	5.325	9.302	28.649	90.01	97.21	90.15	1407.737
SiSiSiSi	5.325	9.305	28.658	89.95	97.23	90.22	1408.662
Exp.	5.349	9.255	28.890	90.00	97.12	90.00	1419.171

theoretical models give smaller volumes of the elementary cell in comparison to the experimental one. The unit cell angles are very close to the experimental ones. One can see from Table 1 that the parameters and volume closest to the experimental data is for the SiSiSiSi model – it is the case where silicon atoms in the tetrahedra are closest to the interlayer Mg^{2+} cations in the unit cell. The largest deviations were observed for the opposite case when Al atoms coordinate all interlayer Mg^{2+} cations. With increasing Si coordination of the interlayer Mg^{2+} cation, differences to the experiment become smaller.

Energetic stabilization

The energetic stabilization with respect to the T···Mg···T′ ordering will be discussed in this paragraph. Table 2 displays differences in electronic energies of all six models studied (for both cases – with fixed and optimized unit cells) related to the lowest calculated energy (−955.07989 eV for the SiSiSiSi/optimized cell model). Comparison of calculated energies shows that the unit-cell relaxation leads to an additional energetic stabilization of about 1–3 kJ mol^{-1}. This stabilization is small, corresponding to the small changes of the unit-cell parameters related to the fixed unit cell (Table 1). The order of stabilization increases consecutively from the AlAlAlAl to the SiSiSiSi model for both types of structural relaxation. Most remarkable is the fact that the most stable model is that where silicon atoms are the closest to the interlayer Mg^{2+} cations (SiSiSiSi model). This is in contrast to the assumption of Shirozu and Bailey (1966) and Slade et al. (1985), who supposed that the interlayer Mg^{2+} cations are localized closest to the Al substitutions in the interlayer space due to smaller Coulombic repulsion between $Al^{3+}···Mg^{2+}$ cations than between $Si^{4+}···Mg^{2+}$. However, we observed that the T···Mg^{2+} distance is shorter just for the SiSiSiSi model (averaged value is of 4.348 Å) than for the AlAlAlAl model (averaged value is of 4.401 Å). Thus, Coulomb interaction between Si/Al and Mg cations does not play the crucial role in determining the relative energetic stabilizations of the different models. We suggest that the larger polarization of the $O_b···H–O$ hydrogen bonds between the 2:1 layer and the water layers by Si^{4+} cations than by Al^{3+} cations could be responsible for the relative stabilities. Moreover, we should mention that in the natural Llano vermiculite only half of the concentration of the interlayer Mg^{2+} cations is found as

Table 2 Relative electronic energies (in kJ mol^{-1}) of all models studied calculated for fixed and optimized unit cells

Model	Fixed unit cell	Optimized unit cell
AlAlAlAl	17.22	16.11
SiAlAlAl	13.04	10.07
SiAlSiAl	10.19	6.90
SiAlAlSi	8.47	6.82
AlSiSiSi	8.22	3.80
SiSiSiSi	3.20	0.00

compared to our models, and that therefore the balance between attractive and repulsive forces could be different there.

Conclusions

Six different models of the vermiculite structure with excess charge of −2 per structural formula were studied using the DFT approach and applying periodic boundary conditions. The models differ by the T···Mg···T′-T″···Mg···T‴ ordering where T, T′, T″ and T‴ are the closest central cations in the opposite tetrahedral sheets of the 2:1 layers. Two types of the structural relaxations were performed – atomic position relaxation with fixed experimental unit-cell parameters and relaxation of atomic positions and unit-cell parameters together. Observed changes of the unit-cell parameters are very small compared to the experimental values. Best accord with experimental data was observed for the SiSiSiSi model. Analysis of bond distances within the 2:1 layer showed relatively good agreement with the experimental data (Shirozu and Bailey 1966). The dominating factor affecting the layer stacking is the formation of very strong hydrogen bonds (bond length about 1.5 Å) between water molecules coordinating the interlayer Mg^{2+} cations and the basal oxygen atoms of the 2:1 layers. Mg^{2+} cations are located above and below central tetrahedral cations T and T′ in such way that T···Mg^{2+}···T′ is practically collinear. The second type of hydrogen bond is formed between water molecules from the two water layers coordinating the Mg^{2+} cations.

Comparison of the calculated total electronic energies showed that the most stable model is that with the SiSiSiSi arrangement. This means that the silicon atoms in the tetrahedral sheets are closest to the interlayer Mg^{2+} cations in the unit cell. We suggest that the polarization of the $O_b···H–O$ hydrogen bonds by Si^{4+}

cations is the main reason for the highest stabilization of the SiSiSiSi model in comparison to the others.

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