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A MOLECULAR-ORBITAL STUDY OF DISTORTIONS IN THE LAYER STRUCTURES BRUCITE, GIBBSITE AND SERPENTINE

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ABSTRACT

A CNDO/2 molecular orbital study of the distortions in layer structures shows that octahedral cluster calculations predict the observed flattening of the cation-containing octahedral sheets in brucite and gibbsite. The shared edges involving O–H bonds oriented perpendicular to the dioctahedral sheet in gibbsite are calculated, as observed, to be shorter than the shared edges involving O–H bonds oriented parallel to the sheet. A silicate-ring cluster calculation predicts that a ditrigonal ring like that in tourmaline is more stable than a hexagonal ring of the type found in beryl. A cluster calculation for a silicate ring articulated to three Mg-containing octahedra is used to model structural distortions in serpentine. The close correspondence between the observed and calculated distortions indicates that the layer flattening and ditrigonal distortions unique to layer structures are controlled primarily by short-range bonding forces.

SOMMAIRE

L'étude des difformités des structures en couches par analyse (CNDO/2) d'orbitales moléculaires indique que les calculs faits sur agrégats octaédriques prédisent l'aplatissement, dans la brucite et la gibbsite, des feuillets d'octaèdres entourant les cations. Dans la gibbsite, la longueur calculée des arêtes communes qui se terminent par une liaison O–H dépend de l'orientation de cette liaison: conformément aux faits, elle est plus courte lorsque la liaison O–H est normale au plan du feuillet dioctaédrique que lorsqu'elle lui est parallèle. Le calcul d'agrégat des anneaux de silicate prévoit qu'un anneau ditrigonal, tel celui de la tourmaline, est plus stable qu'un anneau hexagonal, du type béryl par exemple. Un calcul analogue, appliqué à un anneau de silicate articulé à trois octaèdres à Mg, mène à concevoir des modèles pour les difformités structurales de la serpentine. L'accord entre la difformité observée et celle que prédit le calcul montre bien que l'aplatissement de la couche et la distorsion ditrigonale caractéristiques des structures en couches résultent, en ordre principal, de forces de liaison à petite distance.

(Traduit par la Rédaction)

INTRODUCTION

A number of important studies have been devoted to clarifying the distortions in layer structures using methods based on ionic interactions and Pauling's rules (Pauling 1929, 1930, Newnham & Brindley 1956, Radoslovich 1963, Donnay *et al.* 1964, Bailey 1967, McCauley & Newnham 1971, Hazen & Wones 1972, Wicks & Whittaker 1975, Giese 1976, Appelo 1977, 1978). These studies indicate that flattening of the octahedral sheet is due to shortening of shared edges and that the distortion of articulated tetrahedral and octahedral sheets from ideal geometries is due to an intrinsic misfit between the two sheets. The present study was undertaken to see whether these distortions are predicted by semi-empirical molecular-orbital-cluster calculations that include both ionic and covalent interactions.

CNDO/2 MOLECULAR-ORBITAL CALCULATIONS

In recent years, solid-state molecular-orbital (MO) studies have provided considerable insight into the visible, UV and X-ray emission and photoelectron spectra and the geometries of a number of minerals (Tossell & Gibbs 1977, Meagher *et al.* 1979). The MO calculations undertaken in this study were made with computer program CNINDO (QCPE Program 141) obtained from the Quantum Chemistry Exchange, Indiana University. A minimum-valence *sp* basis was used for O, F, Mg, Al and Si and a *s* basis was used for H. The CNDO/2 method (Pople et al. 1965, Pople & Beveridge 1970) has been widely used for cluster calculations in organic and inorganic chemistry (*cf.*, Santry 1968, Gordon 1969). Marsh & Gordon (1976) examined the capability of the method for predicting bond

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angles in molecules with third-period elements and found that it reproduced bond-angle trends reasonably well. Recent studies on shared-edge distortions for silica-W (Tossell & Gibbs 1976a), several olivine structure-types (Tossell & Gibbs 1976a, b, McLarnan *et al.* 1979) and andalusite (Hill *et al.* 1979) have shown that CNDO/2 theory can also predict shared-edge lengths with reasonable accuracy. These results and others indicate that molecular-orbital calculations for clusters isolated from solids (Messmer 1977) can provide important insights into the bonding forces that govern a local configuration in a solid.

TRIOCTAHEDRAL-LAYER DISTORTIONS AND CALCULATIONS FOR BRUCITE, $Mg(OH)_2$

The brucite structure consists of a layered sequence of hexagonal closest packed monolayers of hydroxyl anions (Aminoff 1921, Zigan & Rothbauer 1967). The octahedra in alternate layers in the sequence are filled by Mg atoms to form trioctahedral sheets of edge-sharing MgO_6 octahedra. The Mg–O bonds are identical (2.10 Å), and adjacent trioctahedral sheets in the sequence are held together by weak-bonding forces. Insofar as the six shared edges of each octahedron are shorter than the unshared ones, the trioctahedral sheet is flattened. Moreover, as the upper and lower triangular faces of each octahedron in the sheet are related by $\bar{3}m$ point-symmetry, we may conclude that the flattening of the sheet was accomplished by trigonal compression.

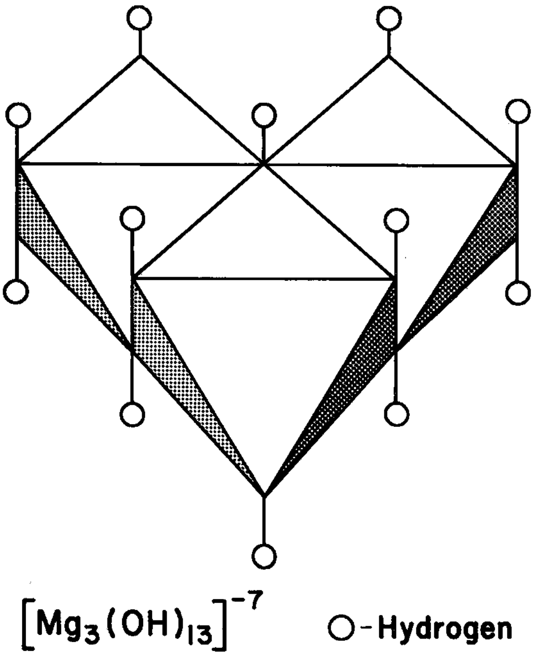

FIG. 1. A $[Mg_3(OH)_{13}]^{7-}$ trimer used to model the layer flattening in brucite. Each octahedron in the trimer contains a Mg atom with oxygen atoms positioned at each octahedral corner. H atoms are depicted as open circles at the ends of O–H bonds set perpendicular to the plane defined by the three Mg atoms.

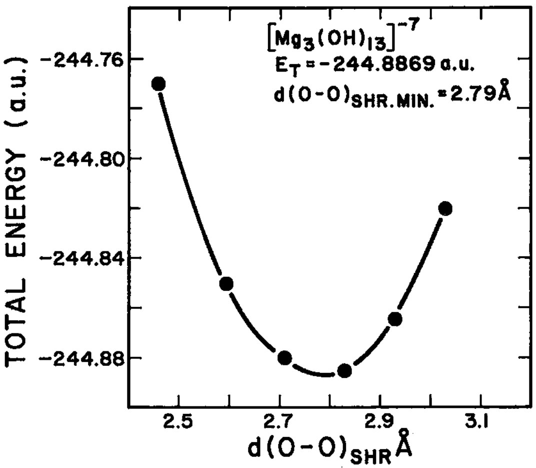

FIG. 2: Total energy (atomic units) of the $[Mg_3(OH)_{13}]^{7-}$ trimer (Fig. 1) plotted as a function of the shared-edge length, $d(O–O)_{shr}$. One atomic unit (*a.u.*) = 627 kcal/mole.

To learn whether CNDO/2 theory can predict the shared octahedral-edge lengths and hence the thickness of the trioctahedral sheet, we made a series of calculations on an edge-sharing $[Mg_3(OH)_{13}]^{7-}$ trimer (Fig. 1). In the calculations, all O–H bonds were set perpendicular to the plane of the cluster at $d(O–H) = 1.0$ Å, $d(Mg–O)$ was fixed at 2.10 Å and the shared

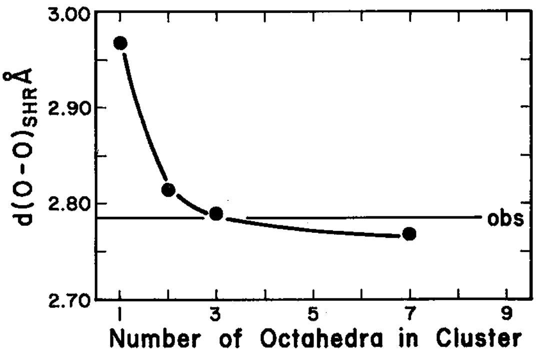

FIG. 3: Minimum-energy shared-edge length, $d(O–O)_{shr}$ *versus* the number of Mg-containing octahedra comprising a brucite-type cluster.

edges were varied from 2.45 to 3.05 Å. Within the constraints of $\bar{3}m$ point-symmetry, each octahedron in the trimer was flattened by trigonal compression as the shared and the unshared equatorial edges were shortened. The total energy for each trimer plotted against the length of the shared edge, $d(\mathrm{O} \ldots \mathrm{O})_{\mathrm{shr}}$, shows a minimum in total energy at 2.79 Å (Fig. 2) in agreement with the shared-edge length (2.78 Å) recorded for brucite (Zigan & Rothbauer 1967). This requires flattening of the three octahedra to a thickness of 2.12 Å compared with 2.11 Å observed in brucite.

The close correspondence between the distortion of the trioctahedral sheet in brucite and that indicated by the cluster calculation suggests that the shortened shared edges and the flattened trioctahedral sheet in brucite are produced primarily by short-range bonding forces. If the distortions of the sheet were produced by long-range forces, then we would not expect the trimer to give a satisfactory prediction of shared-edge lengths and layer flattening. Furthermore, if short-range forces control the distortions, then we may expect that the shared-edge length of minimum energy should converge rapidly as the size of the cluster is increased. As a test, minimum-energy edge lengths were calculated for three additional clusters, *i.e.*, one consisting of a single octahedron $[\mathrm{Mg(OH)_6}]^{4-}$, a dimer consisting of two edge-sharing octahedra $[\mathrm{Mg_2(OH)_{10}}]^{6-}$ and a third consisting of seven edge-sharing octahedra $[\mathrm{Mg_7(OH)_6F_{18}}]^{10-}$. The resulting minimum-energy edge lengths, plotted in Figure 3 as a function of the number of octahedra in the cluster, show that the minimum-energy shared-edge length approaches a value slightly less than that observed in brucite as the cluster size is increased.

For the cluster consisting of seven edge-sharing octahedra, F was used in place of OH at the periphery of the cluster to reduce the number of atoms in the cluster and therefore the time and cost of the calculation. Calculations involving identical clusters for which peripheral OH was replaced by F indicate that this replacement has little effect on the position of minimum-energy parameters such as shared-edge lengths.

DIOCTAHEDRAL-LAYER DISTORTIONS AND CALCULATIONS FOR GIBBSITE, $\mathrm{Al(OH)_3}$

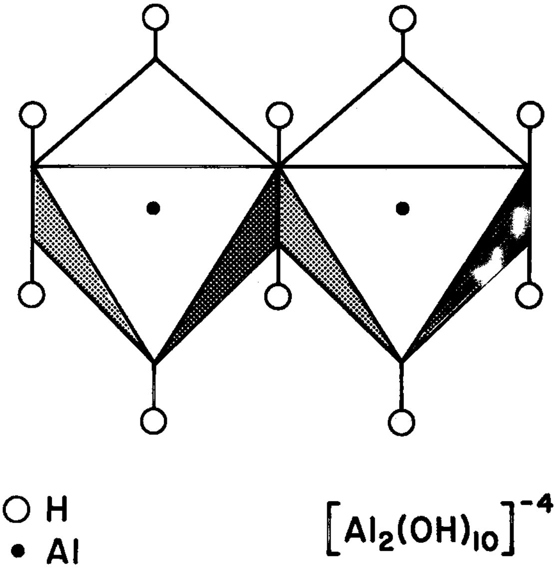

FIG. 4: An $[\mathrm{Al_2(OH)_{10}}]^{4-}$ dimer used to model the distortions in the octahedral layer of gibbsite. The corners of each octahedron are occupied by hydroxyl groups, and the centres are occupied by Al. H atoms associated with the hydroxyl groups are placed at the ends of O–H bonds set perpendicular to the plane of the dimer.

Gibbsite consists of monolayers of OH anions forming a sequence of dioctahedral sheets, weakly bonded together as in brucite (Megaw 1934, Saalfeld & Wedde 1974). However, unlike brucite in which all of the available octahedral sites in every other sheet in the sequence are filled, two-thirds of the sites in gibbsite are filled by Al. Accordingly, each $\mathrm{AlO_6}$ octahedron in the dioctahedral sheet shares only three of its equatorial edges. Shared edges are shorter than the unshared, and the octahedral sheet is flattened by a twisted trigonal compression (Newnham 1961) (*i.e.*, the upper and lower triangular faces of each $\mathrm{AlO_6}$ octahedron are rotated ~ 5° in opposite senses) rather than by trigonal compression (no twisting) as observed in brucite.

As it is also possible to shorten the shared edges of an octahedron without flattening it, a series of calculations was made for an edge-sharing $[\mathrm{Al_2(OH)_{10}}]^{4-}$ dimer (Fig. 4) in which both shared-edge length and thickness were varied. As before, all O–H bonds were set perpendicular to the plane of the cluster at $d(\mathrm{O{-}H}) = 1.0$ Å. In addition, $d(\mathrm{Al{-}O})$ was fixed at 1.895 Å and a local point-symmetry of 32 was assumed for each octahedron. The total energy of the dimer, calculated as the shared-edge length was varied between 2.30 and 2.50 Å and as the dimer thickness was varied between 1.98 and 2.18 Å, is plotted and contoured in Figure

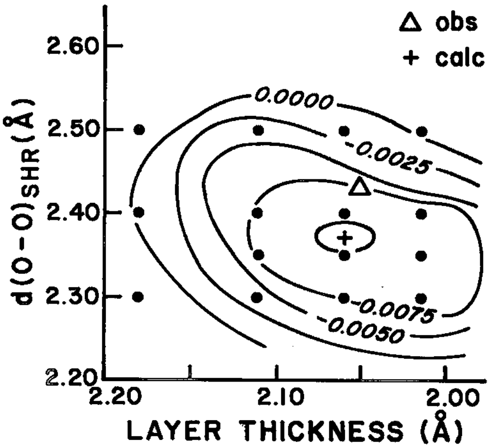

FIG. 5: Map of isoenergy curves (of –191.8675 *a.u.*) for the $[Al_2(OH)_{10}]^{4-}$ dimer depicted in Figure 4 constructed as a function of shared-edge length, $d(O–O)_{shr}$ and thickness of dimer. Calculations were completed for geometries indicated by points.

5. The resulting potential-energy surface shows that the dimer has its lowest energy when its shared-edge length is 2.38 Å and its thickness is 2.06 Å. These values are in satisfactory agreement with the averaged shared-edge length (2.44 Å) and thickness (2.05 Å) observed for the dioctahedral sheet in gibbsite.

There are two distinct types (denoted I and II) of shared edge in gibbsite that require further examination (Giese 1976). The type-I edges involve hydroxyl groups with O–H bonds oriented perpendicular to the dioctahedral sheet, whereas type-II edges involve hydroxyl anions with O–H bonds oriented parallel to the sheet. To explore the effect of the orientation of the O–H bond on the minimum-energy shared-edge length, we made calculations for $[Al_2(OH)_{10}]^{4-}$ dimers with type-I and type-II shared edges where O–H bonds involved in the unshared edges were set at $d(O–H) = 1.0$ and parallel to the Al–O bond. In addition, the thickness of the dimer was fixed at the minimum-energy value obtained in Figure 5. The calculations yielded the following minimum-energy shared-edge lengths: type I 2.41 Å, type II 2.48 Å. These values are in good agreement with the shared-edge lengths observed for gibbsite (type I 2.42 Å, type II 2.46 Å: Saalfeld & Wedde 1974), predicting that the type-II edges should be longer than type-I edges.

TETRAHEDRAL-LAYER DISTORTIONS AND CALCULATIONS

The structure of a number of sheet silicates consists of an octahedral sheet articulated to one or two tetrahedral sheets. The octahedral sheets may have all of their octahedra filled as in brucite, or two-thirds filled as in gibbsite. Ideally, the tetrahedral sheet consists of Si-rich tetrahedra corners linked together into a sheet of hexagonal rings. For our calculations, a six-membered ring of $Si_6O_6(OH)_{12}$ composition was chosen as a representative cluster for the sheet. Within the ring the point symmetry of each silicate ion was $\bar{4}3m$ with $d(Si–O)$ fixed at 1.62 Å and with H atoms attached at 1.0 Å from each non-bridging oxygen so that $\angle SiOH = 180°$. Total-energy calculations were made for a set of such rings with tilt angles γ varied from the case where the ring possesses $6/mmm$ point-symmetry ($\gamma = 0°$) to the case where $\gamma = 50°$ (Fig. 6). The symmetry of the cluster was maintained in the calculations at $6mm$ for tilt angles $\gamma > 0$. Despite the minimization of the electrostatic energy when $\gamma = 0°$ (Zoltai & Buerger 1960), the total energy shows a local maximum for this tilt angle (Fig. 7), indicating that a six-membered ring like that in beryl is less stable than that of the type found in tourmaline, where $\gamma > 0°$. On the other hand, the total energy shows a minimum value when $\gamma = 36.8°$ compared with a value of 35.3° for the case in which the bases of the tetrahedra are all coplanar. The minimum energy γ value of 36.8° requires a slight tilting of the bases of the tetrahedra out of the plane of the six-membered ring. In addition, it requires an Si–O–Si angle of 140°, in close agreement with the mean value (~144°) recorded for a large number of silicates (Tossell & Gibbs 1978), and the minimum-energy angle (138°) obtained in a SCF *ab initio* MO calculation for $H_6Si_2O_7$ (Newton & Gibbs 1979).

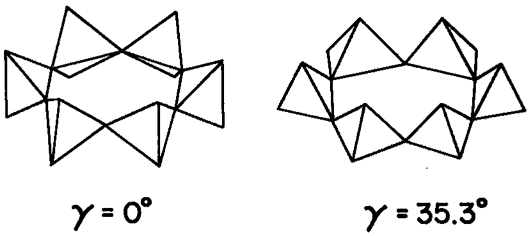
$\gamma = 0°$ $\gamma = 35.3°$

FIG. 6: $Si_6O_6(OH)_{12}$ silicate-ring clusters illustrating tilt angles of 0° (left) and 35.3° (right). Si atoms (not shown) occupy the centre of each tetrahedron, and oxygen atoms are located at each tetrahedral corner. H atoms (not shown) are attached to the non-bridging atoms at a distance of 1 Å.

In an ideal tetrahedral sheet of hexagonal

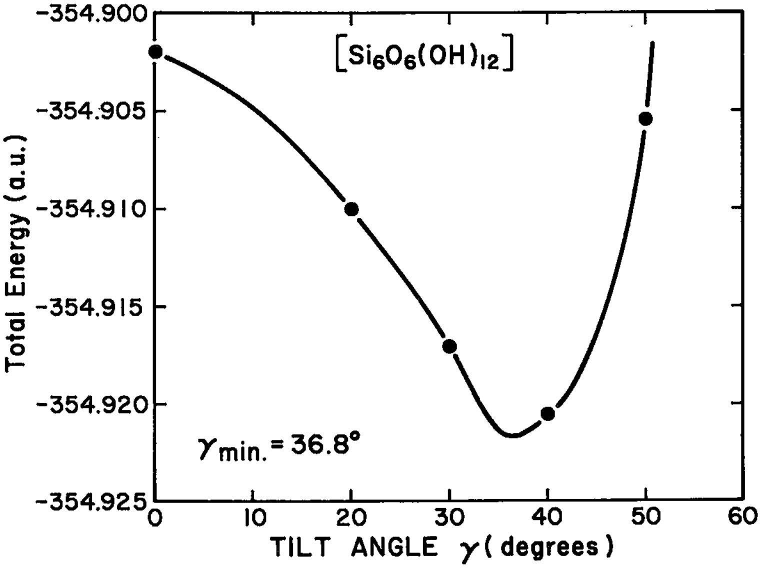

FIG. 7: Total energy of a $Si_6O_6(OH)_{12}$ cluster *versus* the tilt angle of the tetrahedra (two clusters illustrating tilt angles of $\gamma = 0°$ and $35.3°$ are shown in Fig. 6). For symmetry reasons, the energy curve is symmetrical about $\gamma = 0°$.

rings with $6mm$ symmetry, the tetrahedra are unrotated and their bases are coplanar when $\gamma = 35.3°$. When alternate tetrahedra are rotated in + and − directions about the sheet normal through a turn angle of α (Radoslovich 1961), the sheet may be distorted into an array of ditrigonal rings. These ditrigonal distortions were modeled in our calculations by a $Si_6O_6(OH)_{12}$ ring with γ set at 35.3° (Fig. 8). As before, the local symmetry of each tetrahedron in the ring was $\bar{4}3m$ with d(Si–O) = 1.62 Å, d(O–H) = 1.0 Å and ∠SiOH = 180°.

In the calculations, the symmetry of the ring was preserved at $3m$ point-symmetry when $\alpha \neq 0$ and $6mm$ point-symmetry when $\alpha = 0°$. The total energy of the ring shows a minimum at $\alpha = 16°$ when plotted against α (Fig. 9) rather than 0° as expected from electrostatic considerations. This unexpected result shows that the ring has an intrinsic ditrigonal character, irrespective of octahedral articulation considerations discussed below. Calculations for a six-membered ring of $Si_6O_6F_{12}$ composition yield a minimum α value of 17° and suggest that the replacement of OH by F has little effect on the minimum-energy α value.

SHEET ARTICULATION AND CALCULATIONS FOR SERPENTINE, $Mg_3Si_2O_5(OH)_4$

A cluster of $[Mg_3F_6(OH)_7Si_6O_6F_6]^-$ composition (Fig. 10) was chosen as a representative block of a *T–O* layer like that in serpentine (Wicks & Whittaker 1975). All Mg–O and Mg–F distances in the cluster were fixed at 2.10 Å, d(Si–O) was fixed at 1.62 Å and the local point-symmetry of each tetrahedron in the

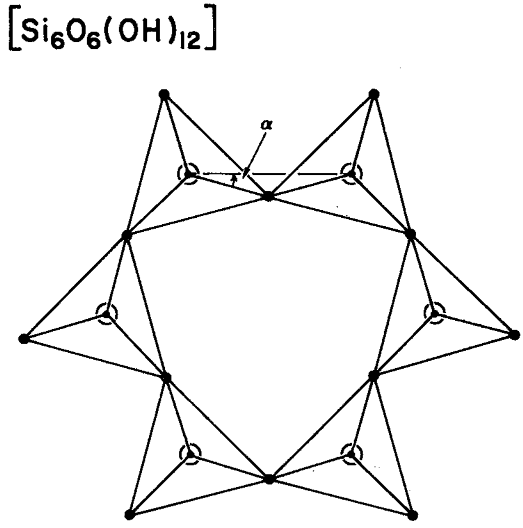

FIG. 8: A six-membered $Si_6O_6(OH)_{12}$ cluster showing an α angle of 15° when the bases of the tetrahedra all lie in a plane (*i.e.*, $\gamma = 35.3°$) (see Fig. 6 for description of cluster).

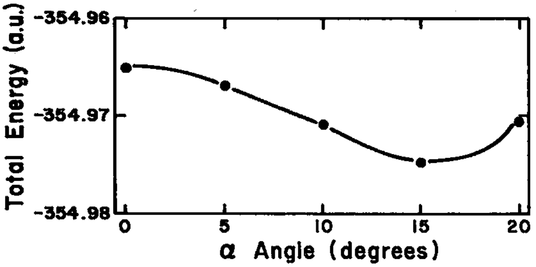

FIG. 9: Total energy of a $Si_6O_6(OH)_{12}$ cluster *versus* the tetrahedral rotation angle α. For symmetry reasons, the energy curve is symmetrical about $\alpha = 0°$.

ring was constrained to be $\bar{4}3m$. The octahedral trimer in the cluster was constructed from a basal monolayer of fluorine atoms and an upper monolayer of oxygen atoms. Hydrogen atoms were attached to each oxygen in the upper layer at a distance of 1.0 Å. The O–H bond formed at the centre of the upper layer was directed away from the monolayer toward the centre of the silicate ring, whereas the remaining O–H bonds were set parallel to the plane and directed away from the cluster. Fluorine atoms were attached to the outermost corners of each tetrahedron at a distance of 1.62 Å from Si, and oxygen atoms were used to bridge the tetrahedra together into a six-membered ring.

Total-energy calculations were made for the cluster as the α angle was varied between -6° and +6°, preserving $3m$ point-symmetry. By maintaining constant bond-lengths, planar monolayers and $3m$ point-symmetry in the calculations, the minimum-energy α value will be dependent upon the shared-edge length, as the degree of flattening of the octahedra as well as the twisting of the tetrahedra are linked to the shared-edge lengths. The resulting E_T values plotted against α in Figure 11 show a minimum energy when $\alpha = -2.1°$, which corresponds to an octahedral thickness of 2.28 Å and a shared-edge length of 2.88 Å. Unfortunately, lack of suitable crystals for a structural determination precludes a comparison of these values with those in serpentine. Nevertheless, a comparison can be made with the values provided by a structural analysis of talc (Rayner & Brown 1973), which consists of a brucite-like sheet articulated between two tetrahedral sheets to form a *T–O–T* layer. Despite the sandwiching of the brucite sheet between two tetrahedral sheets, the thickness (2.22 Å) and average shared-edge lengths (2.80 Å) of the trioctahedral layer are of the correct order. Although the magnitude of the α angle (+3.4°) in talc is in reasonable agreement with the predicted value (–2.1 Å), the sense of the predicted value requires a rotation of the bridging oxygens away from the nearest metal atoms in the octahedral sheet. In contrast, positive α angles, which require a rotation of the bridging oxygen toward nearest metal atoms in the octahedral layer, seem to be the rule rather than the exception in *T–O–T*-layer mica structures (Bailey 1967).

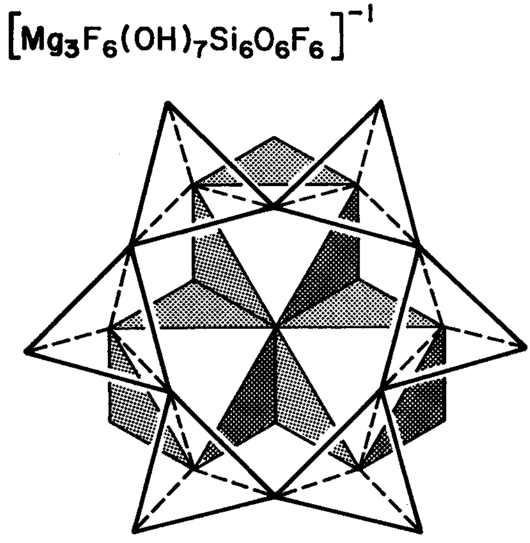

FIG. 10: A $[Mg_3F_6(OH)_7Si_6O_6F_6]^-$ cluster comprising a six-membered silicate ring articulated to an octahedral trimer of Mg-containing octahedra.

To obtain larger α values while maintaining reasonable shared-edge lengths in the octahedral sheet, we carried out total-energy calculations for the same $[Mg_3F_6(OH)_7Si_6O_6F_6]^-$ cluster but with d(Si–O) = 1.68 Å. Figure 12 shows two minima roughly symmetrical about $\alpha = 0°$, with the one at $\alpha = -12.3°$ showing a lower energy by about 0.003 atomic units. This result agrees with an α value of –8° recorded for an amesite with d(Si,Al–O) = 1.66 Å (Jahanbagloo & Zoltai 1968).

The *T* and *O* sheets comprising the *T–O* layer in serpentine may also be represented by a second cluster of $[Mg_4F_{12}(OH)_3Si_3O_3F_5]^{6-}$ composition (Fig. 13). This cluster was derived by dividing the $[Mg_3F_6(OH)_7Si_6O_6F_6]^-$ cluster (Fig. 10) along a vertical mirror plane and adding two Mg-containing octahedra to the *O* sheet. The bond lengths were fixed during the optimization of the geometry, and the symmetry constraints were identical with those used for $[Mg_3F_6(OH)_7Si_6O_6F_6]^-$ cluster. In the $[Mg_3F_6(OH)_7Si_6O_6F_6]^-$ cluster, tetrahedra articulate to

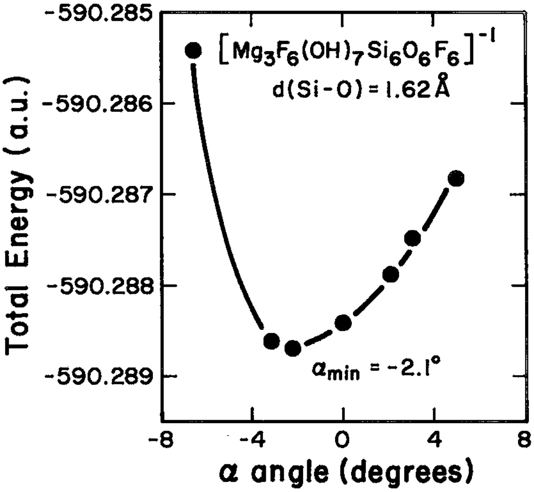

FIG. 11: Total energy of a $[\mathrm{Mg_3F_6(OH)_7Si_6O_6F_6}]^-$ cluster with d(Si–O) = 1.62 Å *versus* the tetrahedral-rotation angle α. The symmetry of the cluster was maintained at $3m$ as α was varied from -6° to 6° and as shared edges and the thickness of the octahedral trimer were decreased.

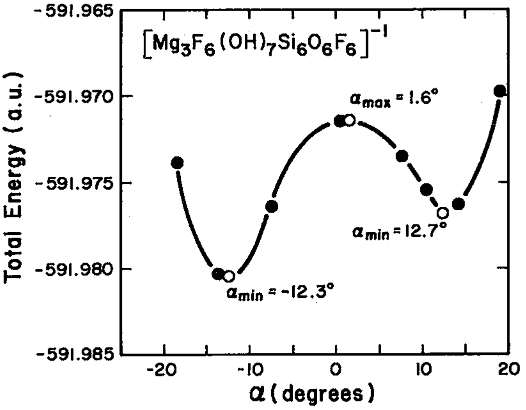

FIG. 12: Total energy of a $[\mathrm{Mg_3F_6(OH)_7Si_6O_6F_6}]^-$ cluster with d(Si–O) = 1.68 Å *versus* the tetrahedral-rotation angle. Open circles plot positions of the calculated minima and maximum.

the octahedral sheet only at the periphery of the upper monolayer, whereas in the derivative cluster the tetrahedra articulate to points somewhat more interior to the upper monolayer of the octahedral sheet. This cluster also better models the effects of the bridging oxygens of the tetrahedra sheet moving over the filled octahedral sites, as 4 of the 7 oxygens forming the bases of the tetrahedra move over filled octahedra with $+\alpha$ angle rotation whereas only 3 of 12 move over filled octahedra with $+\alpha$ rotation in the $[\mathrm{Mg_3F_6(OH)_7Si_6O_6F_6}]^-$ cluster. Calculation of the total energy of this $[\mathrm{Mg_4F_{12}(OH)_3Si_3O_3F_5}]^{6-}$ cluster as a function of α rotation for d(Si–O) = 1.62 Å results in a minimum at $\alpha = -3.9°$ and for d(Si–O) = 1.68 results in minima at +10.6° and –13.8°, which are very similar to the results of the earlier serpentine cluster.

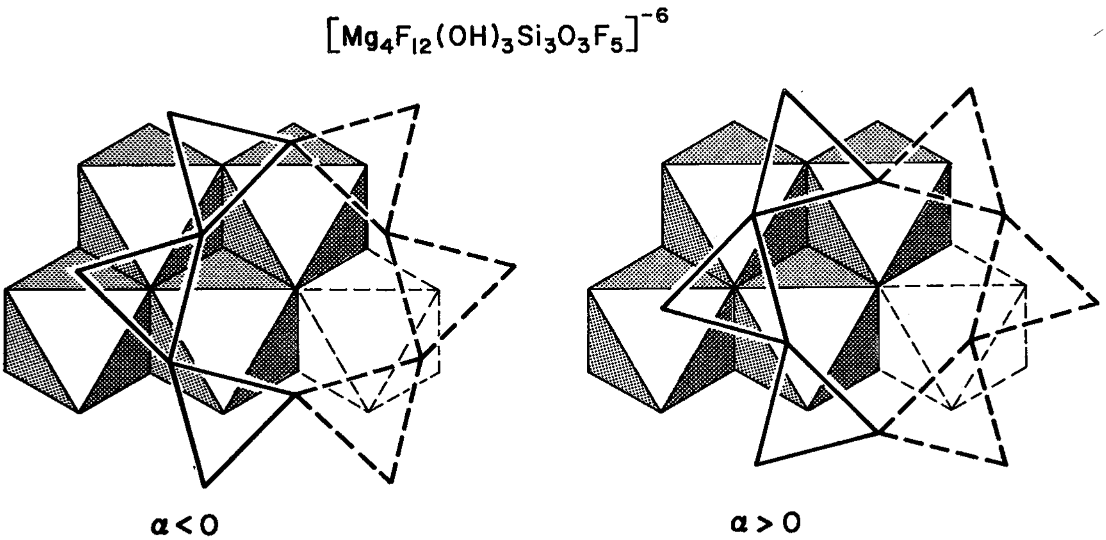

FIG. 13: A $[\mathrm{Mg_4F_{12}(OH)_3Si_3O_3F_5}]^{6-}$ cluster (outlined in solid lines) consisting of four edge-sharing Mg-containing octahedra articulated to three silicate tetrahedra. The dashed lines are included to show the structural similarity of the cluster with that of the $[\mathrm{Mg_3F_6(OH)_7Si_6O_6F_6}]^-$ cluster shown in Figure 10.

In both clusters the minimum energy occurs at negative α values, in contrast to most observed T–O–T α rotations, which are positive. This could result because the sense of tetrahedral rotation is not controlled by factors such as the interaction between the tetrahedral bridging oxygens and octahedral cations but by interlayer effects not modeled by these small clusters. Also, these clusters are highly idealized, and points of the minimum-energy configuration may be model-dependent.

CONCLUSIONS

Molecular-orbital calculations carried out for distorted clusters isolated from brucite and gibbsite predict correct-order minimum-energy octahedral-layer thicknesses and shared-edge lengths, $d(\mathrm{O–O})_{\mathrm{shr}}$:

	brucite		gibbsite	
	obs. Å	pred. Å	obs. Å	pred. Å
thickness	2.11	2.12	2.05	2.06
$d(\mathrm{O–O})_{\mathrm{shr}}$	2.78	2.79	2.44	2.38

In addition, the minimum-energy configuration of a six-membered ring of silicate tetrahedra is predicted to conform with the ditrigonal array of tetrahedral rings observed for a number of sheet silicates. Calculations for a distorted cluster consisting of a six-membered silicate ring articulated to a trimer of three edge-sharing Mg-containing octahedra predict a minimum-energy α angle for serpentine of –2.1°, an octahedral layer thickness of 2.28 Å and a shared-edge length of 2.88 Å.

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