

CALCULATION OF ELECTROSTATIC INTERLAYER BONDING ENERGY AND LATTICE ENERGY OF POLAR PHYLLOSILICATES: KAOLINITE AND CHLORITE

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Abstract—The electrostatic lattice energy of polar phyllosilicates can be calculated when a correction term E_{corr} equal to $-2\pi\mu^2/V$ is taken into account, where μ is the dipole moment of a slice $d(001)$ and V is the molecular volume. The interlayer bonding energy can be obtained by Giese's method, if the energy of separation of the layers over a distance Δ is plotted against $1/[d(001) + \Delta]$. Thus, for a polar chlorite the interlayer bonding energy is 69.8 kJ/unit cell. Using the Madelung method, the interlayer bonding energy of slices of kaolinite having a thickness of $d(001)$ is 84 kJ/mole. Similarly the interlayer bonding energy of slices having a thickness $d(020)$ is 2520 kJ/mole. To avoid the instability of the outer slices of the crystal caused by the cooperating dipole moments of all slices, the hypothesis was made that the atoms have in reality reduced charges and that the charge reduction is such that the dipole moment becomes zero. The adopted charges lower the interlayer bonding energy to as little as 14 kJ/mole. The interlayer interaction of slices of fluorkaolinite with thickness $d(001)$ is repulsive. Crystals of a polar chlorite must be bounded either by incomplete hydroxide layers or by layers onto which charge-compensating anions are adsorbed. Polarity makes cleavage in chlorite more difficult.

Key Words—Chlorite, Electrostatic energy, Interlayer bonding, Kaolinite, Lattice energy.

INTRODUCTION

The electrostatic part of the interlayer bonding energy of a number of phyllosilicates with a polar structure has been studied in recent years: kaolinite, dickite, and nacrite (Giese, 1973), cronstedtite (Giese, 1978), amesite (Giese, 1980) and chlorite (Bish and Giese, 1981). With nonpolar chlorites Bish and Giese (1981) found that the change in electrostatic lattice energy upon separation of the layers became constant beyond a separation distance of about 7 Å, in accordance with previous results for 2:1 phyllosilicates like talc and pyrophyllite (Giese, 1975), and muscovite, phlogopite, lepidolite, and margarite (Giese, 1978). For the polar structures mentioned above, the absolute value of the lattice energy continued to decrease with increasing separation distance, but a limit for an infinite separation distance was not obtained (Giese, 1973, 1978, 1980; Bish and Giese, 1981). It is the aim of the present paper to explain these results and to provide a solution to the calculation of the electrostatic part of the interlayer bonding energy.

THEORY

A crystal structure can be considered as a stacking of slices, each having a thickness $d(hkl)$. When the slices are separated by an infinitely large distance so that there is no interaction energy between the slices, the lattice energy, E_{cr} , is equal to the energy of one slice, denoted by E_{sl} . The difference has been called the attachment

energy, E_{att} , defined as the energy released when one slice of thickness $d(hkl)$ is attached to a face (hkl) that bounds the crystal (see e.g., Hartman, 1973, 1978). Thus:

$$E_{\text{cr}} = E_{\text{sl}} + E_{\text{att}} \quad (1)$$

If E_i is the interaction energy per formula unit between the zero'th and the i 'th slice,

$$E_{\text{att}} = \sum_i E_i \quad (2)$$

As pointed out earlier (Jenkins and Hartman, 1979) the interlayer bonding energy obtained by Giese's method is actually the value of E_{att} and not E , the interaction energy between two neighboring slices in the crystal.

If the slices have a dipole moment μ , Eq. (1) no longer holds and must be replaced by:

$$E_{\text{cr}} = E_{\text{sl}} + E_{\text{att}} + E_{\text{corr}} \quad (3)$$

where E_{corr} is a correction term necessitated by the slice-wise summation used to obtain E_{cr} (Hartman, 1982). Smith (1981) and Hartman (1982) found that

$$E_{\text{corr}} = -2\pi\mu^2/V \quad (4)$$

where V is the unit-cell volume. Thus, it is clear why Giese's method of calculating interlayer bonding energy fails to produce a constant value. For each separation distance Δ , the correction term E_{corr} has a different value because it is proportional to $1/[d(001) + \Delta]$, and, thus, becomes zero when $\Delta = \infty$. Hence, for

polar structures E_{att} can be found only after infinite separation of the layers, and not after a finite separation of the order of 7 Å, as is the case for layer structures with a zero dipole moment. For polar structures E_{att} can be obtained when the expansion energy, U_{exp} , which is the difference in lattice energy between the non-expanded structure and the expanded structure in which the layers are separated by Δ , is plotted against $1/[d(001) + \Delta]$. In Figure 1 this plot is given for a polar structure of a IIb chlorite, based upon the data presented by Bish and Giese (1981) in their Figure 1. Extrapolation of the last five points to $\Delta = \infty$ yields an energy of 673.4 ± 0.4 kcal/unit cell which is equal to $E_{att} + E_{corr}$.

The correction term for the unexpanded structure is 603.6 kcal/unit cell and leads to a value of E_{att} of about 69.8 kcal/unit cell, comparable to the value of 51.3 kcal/unit cell found by Bish and Giese (1981) for a nonpolar chlorite. The question arises whether an interlayer bonding energy of 69.8 kcal/unit cell is reasonable. If one defines the interlayer bonding energy as the interaction energy between two successive layers, that is E_i , the answer is yes. Also, for polar slices that are infinitely large, $E_i \ll E_i$ when $i > 1$, which means that in practice for slices with $d_{hkl} > 5$ Å, E_{att} is approximately equal to E_i . If one defines the interlayer bonding energy as the energy required to separate an infinitely thick crystal into two halves along the plane (hk), 69.8 kcal/unit cell is not reasonable, because this energy is given by

$$E_s = \sum_i iE_i, \quad (5)$$

which equals E_{att} only if terms with $i \geq 2$ can be neglected, as is indeed the case for nonpolar phyllosilicates. For a polar structure, however, the surface becomes unstable because in the outer layers of the crystal the cooperating dipole moments of all slices will expel the cations at one side and the anions at the other side. Based upon the creation of an induced opposite dipole moment of the crystal, this catastrophe can be avoided by the following remedies: (1) In structures with a three-dimensional network of tightly bonded ions, for example, MgO- and ZnS-type semiconductors, a very slight polarization of all bonds will furnish a volume charge of opposite sign at both ends of the crystal. In this way a dipole moment is obtained that cancels the original one (see e.g., Fripiat *et al.*, 1977). (2) Ions can be removed from the outermost planes or become adsorbed on these planes in structural positions. Eventually both processes could occur; for example, the unstable (111) face of NaCl, bounded by a plane of chloride ions, can be stabilized by removing half of the chloride ions in the outermost plane and by removing one quarter of the sodium ions in the next plane and placing these on top of the chloride plane. If this is carried out in a regular way, the surface consists on the atomic scale of minute cube faces (Hartman, 1959; Nosker *et al.*, 1970).

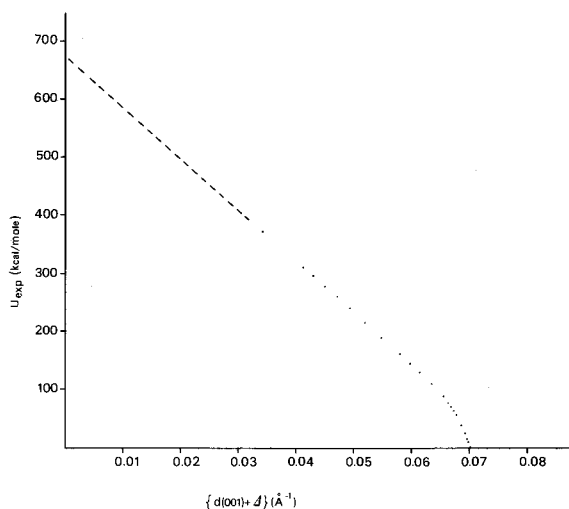


Figure 1. The expansion energy U_{exp} of a polar chlorite as a function of $1/[d(001) + \Delta]$, where Δ is the expansion distance. Data from Bish and Giese (1981). The dotted line gives the extrapolation to infinite expansion.

(3) Quantum chemical calculations show that the electron density distribution within a silicate does not conform with formal charges (Tossell and Gibbs, 1976; de Jong and Brown, 1980; Newton and Gibbs, 1980). The same conclusion follows from an analysis of the phonon spectrum (Iishi, 1976, 1978) and from accurate crystal structure determinations by X-ray or neutron diffraction (Hill, 1979; Sasaki *et al.*, 1980; Fujino *et al.*, 1981; Catti, 1981). In all cases the charges are considerably reduced, because of the partial covalency of the bonds.

For (001) faces of phyllosilicates where no such polarizable bonds between the layers exist, the charge distribution within a layer might be changed so that no dipole moment exists. In the following paragraph this hypothesis is applied to kaolinite, because it has the simplest structure of all polar phyllosilicates.

APPLICATION TO KAOLINITE

In the following analysis, the crystal structure data were taken from Zvyagin (1967) and the positions of the H atoms from Giese and Datta (1973). The slice energy E_{sl} was calculated by the Madelung method (Madelung, 1918; Hartman, 1973) using a computer program ENERGY written by Woensdregt (1971). This method consists essentially of the calculation of electrostatic potentials at ion sites with respect to chains of ions parallel to a certain direction [uvw] in a slice $d(hk)$. For kaolinite a chain of composition $Al_2Si_2O_5(OH)_4$ parallel to [100] was chosen. First, the energy of a slice $d(001)$, $E_{sl}(001)$, was calculated. Then the energy of a double slice with thickness $2d(001)$ was calculated. This energy equals $2E_{sl}(001) + E_1$. Neglecting E_2, E_3 , etc. and using E_{corr} , the lattice energy E_{cr} was calculated from Eq. (3). The energies are listed to 7 decimal places in Table 1 to show the effect of neglecting higher terms E_i .

Table 1. Slice energies E_{s_i} , interaction energies E_i between the zero'th and the i 'th slice, correction energies E_{corr} and lattice energies E_{cr} for kaolinite and fluorkaolinite.

Kaolinite			
Energy type	Slice (001) (kJ/mole)	Slice (020) (kJ/mole)	Slice (001) reduced charges (kJ/mole)
E_{s_1}	58,082.46	56,048.16	35,115.55
E_1	84.82	2520.08	14.38
E_2	—	26.47	-0.19
E_3	—	—	0.06
E_{corr}	438.03	9.52	0.00
E_{cr}	58,604.91	58,604.23	35,129.80
Fluorkaolinite			
Energy type	Slice (001) (kJ/mole)	Slice (020) (kJ/mole)	
E_{s_1}	44,330.66	42,095.03	
E_1	-10.74	2201.25	
E_2	—	21.84	
E_{corr}	12.78	14.01	
E_{cr}	44,332.70	44,332.13	

Eqs. (1) and (3) are quite general and by no means restricted to layers of thickness $d(001)$. Therefore, to corroborate the value found for E_{cr} , the crystal was divided into slices of thickness $d(020)$. Each slice contains the same chain of ions of composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ as used in the foregoing calculations. It was necessary to calculate also E_2 , which could not be neglected. E_2 was found by calculating the total slice energy of three consecutive slices $d(020)$, which equals $3E_{s_1}(020) + 2E_1 + E_2$. According to Eq. (2), $E_{\text{att}} = E_1 + E_2$. The calculated energies are also listed in Table 1.

The attachment energy of (001) was also calculated assuming a charge distribution that leads to a zero dipole moment of a slice $d(001)$. Starting with $q_{\text{Al}} = 3.0 e$ and $q_0 = -1.5 e$, $q_{\text{Si}} = 3.0824 e$, and $q_{\text{H}} = 0.3338 e$. The latter value is quite close to that of the hydrogen atom in water corresponding to the dipole moment of 1.84 D, namely $q_{\text{H}} = 0.332 e$. The results are also shown in Table 1.

DISCUSSION

The results for kaolinite slices $d(001)$ agree reasonably well with those of Giese (1980). According to his Figure 3 an expansion of 10 Å corresponds with an expansion energy of about 82 kcal/mole, or 343 kJ/mole. The correction term E_{corr} amounts to 181 kJ/mole, and the sum, 524 kJ/mole, is close to the sum of $E_1 + E_{\text{corr}}$ in Table 1 (522 kJ/mole). The lattice energies, calculated by using $d(001)$ and $d(020)$ slices, show that E_2 , E_3 , etc. may be neglected. The interlayer bonding energy, if defined as E_1 , is negative for fluorkaolinite $d(001)$ slices. Unless the dispersion energy overcompensates the repulsion, this structure would be unstable, a con-

clusion also reached by Wolfe and Giese (1978) using a different approach.

For normal kaolinite the interlayer bonding energy of $d(001)$ slices is 84 kJ/mole. As this energy is mainly due to two, long hydrogen bonds, the value is too high, which suggests reduced charges. Wieckowski and Wiewióra (1976) calculated the total hydrogen bond energy between kaolinite layers to be 39 kJ/mole. Compared with this value the 14 kJ/mole calculated for the reduced charge possibility seems to be too low. No attempt was made at this stage to maximize E_{cr} by varying the reduced charges under the restriction of a zero dipole moment. It should be noted that the large decrease of E_1 by reducing the charges does not occur in 2:1 micas (Jenkins and Hartman, 1980).

In contrast to kaolinite, a polar chlorite consists of a positively charged hydroxide layer and a negatively charged mica layer making this structure in some ways comparable to a normal mica. When an infinitely thick chlorite crystal is split into two halves along (001) the necessary energy E_s (Eq. (5)) becomes infinite. As a consequence the cleavage trace cannot run between a hydroxide layer and one adjacent mica layer. The net charge of the hydroxide layer must be divided among the two halves of the crystal, i.e., either the cleavage trace shifts from one side of the hydroxide layer to the other, thereby breaking Mg-O or Al-O bonds as well, or it breaks OH bonds whereby the protons stick to the adjacent mica layer and the charge of the hydroxide layer is compensated by the presence of oxygen anions.

Similarly, the outermost layer of a polar chlorite cannot be a complete hydroxide layer. Either half of the layer is present in patches, or potential-compensating anions are adsorbed on top of the layer.

CONCLUSIONS

Interlayer bonding energy and lattice energy of a polar phyllosilicate using an electrostatic point charge model can be calculated when an appropriate correction term for the energy is taken into account. The values of the interlayer bonding energy thus calculated must be considered as upper values, if formal charges are used. It is suggested that the charge distribution in a (001) kaolinite slice is such that the dipole moment vanishes. In a polar chlorite the dipole moment always exists, and thus the structure of the outermost hydroxide layer of a crystal is affected, and cleavage is more difficult than for a nonpolar chlorite.

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(Received 25 August 1982; accepted 28 December 1982)

Резюме—Электростатическая энергия решетки полярных филлосиликатов может быть рассчитана, если учесть коррекционный член $E_{\text{корр}}$ равный $-2\pi\mu^2/V$, где μ является дипольным моментом ломтика $d(001)$ и V является молекулярным объемом. Энергия межслойной связи может быть получена при помощи метода Гиса, если энергию разделения слоев на расстоянии Δ представить графически как функцию $1/[d(001) + \Delta]$. Таким образом энергия межслойной связи молярного хлорита равна 69,8 кДж/элементарная ячейка. Используя метод Моделунга было найдено что энергия межслойной связи ломтиков каолинита толщиной $d(001)$ равна 84 кДж/моль, а энергия межслойной связи ломтиков толщиной $d(002)$ равна 2520 кДж/моль. Для избежания нестабильности внешних ломтиков кристалла, вызванной взаимодействием дипольных моментов всех ломтиков была предложена гипотеза, что в действительности атомы имеют уменьшенные заряды и это уменьшение такое, что дипольный момент становится равным нулю. Принятые заряды снижают энергию межслойной связи до величины так малой как 14 кДж/моль. Межслойное взаимодействие ломтиков флюоркаолинита толщиной $d(001)$ является отталкивающимся. Кристаллы полярного хлорита должны быть связаны или незаполненными гидроокисными слоями или слоями, на которых адсорбируются зарядо-компенсирующие анионы. Полярность делает кливаж в хлорите более трудным. [E.G.]

Resümee—Die elektrostatische Gitterenergie polarer Schichtsilikate kann berechnet werden, wenn ein Korrekturem E_{Korr} gleich $-2\pi\mu^2/V$ berücksichtigt wird, wobei μ das Dipolmoment einer Schicht $d(001)$ und V das Molvolumen ist. Die Zwischenschichtbindungsenergie kann mit Hilfe der Giese-Methode erhalten werden, wenn man die Trennungsenergie der Schichten über einen Abstand Δ gegen $1/[d(001) + \Delta]$ aufträgt. Damit ergibt sich für einen polaren Chlorit eine Zwischenschichtbindungsenergie von 69,8 kJ/Einheitszelle. Wenn man die Madelung-Methode verwendet, beträgt die Zwischenschichtbindungsenergie von Kaolinitsschichten parallel zu $d(001)$ 84 kJ/Mol, während die Zwischenschichtbindungsenergie von Schichten parallel zu $d(020)$ 2520 kJ/Mol beträgt. Um die Instabilität äußerer Schichten des Kristalls, die durch die zusammenwirkenden Dipolmomente aller Schichten verursacht wird, zu berücksichtigen, wurde die Annahme gemacht, daß die Atome in Wirklichkeit reduzierte Ladungen haben, und daß die Ladungsverminderung derartig ist, daß das Dipolmoment null wird. Die angenommenen Ladungen verringern die Zwischenschichtbindungsenergie auf den sehr geringen Wert von 14 kJ/Mol. Die Zwischenschichtwechselwirkung der Schichten von Fluorkaolinit parallel zu $d(001)$ ist abstoßend. Kristalle von einem polaren Chlorit müssen entweder durch unvollständige Hydroxidlagen begrenzt werden oder durch Lagen, auf denen ladungskompensierende Anionen adsorbiert sind. Die Polarität erschwert die Spaltung von Chlorit. [U.W.]

Résumé—L'énergie électrostatique de treillis de phyllosilicates polaires peut être calculée lorsqu'on tient compte d'un terme de correction E_{corr} égal à $-2\pi\mu^2/V$, où μ est le moment dipôle d'une tranche $d(001)$ et V est le volume moléculaire. L'énergie de liaison intercouche peut être obtenue par la méthode de Giese, si l'énergie de séparation des couches sur une distance Δ est relevée vis à vis de $1/[d(001) + \Delta]$. Ainsi, pour une chlorite polaire l'énergie de liaison intercouche est 69,8 kJ/maille mère. En utilisant la méthode Madelung, l'énergie de liaison intercouche de tranches de kaolinite d'une épaisseur de $d(001)$ est 84 kJ/mole. De même, l'énergie de liaison intercouche de couches ayant une épaisseur de $d(020)$ est 2520 kJ/mole. Pour éviter l'instabilité des couches externes du cristal causée par les moments dipôles coopérants de toutes les tranches, on a posé l'hypothèse que les atomes ont en réalité des charges réduites et que la réduction de charge est telle que le moment dipôle devient zéro. Les charges adoptées baissent l'énergie de liaison intercouche jusqu'à une valeur aussi basse que 14 kJ/mole. L'interaction intercouche de tranches du fluor-kaolinite d'une épaisseur $d(001)$ est répulsive. Les cristaux d'une chlorite polaire doivent être limités soit par des couches hydroxide incomplètes ou par des couches sur lesquelles des anions compensant la charge sont adsorbés. La polarité rend le clivage de la chlorite plus difficile. [D.J.]