A quantitative method to calculate the potential energy between unit layers in interstratified minerals

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In the interstratified minerals, the potential energy between unit layers is an important crystal chemistry parameter. In the earlier work, it is usually obtained by qualitative methods. A quantitative method with excessive simplification was suggested in a paper of treating the mineral of valleriite (Li and Cui, 1994). In this note, based on the electrostatic theory and the real mineral structure, the authors propose a method to quantitatively calculate the potential energy between unit layers in the interstratified minerals.

Theory

Assuming that the structure of interstratified mineral consists of alternating unit layers of A and B, which are charged with equivalent positive and negative charges distributed uniformly, respectively. The body charge density and height of layer A and layer B are labelled as ρ_A, ρ_B and c_A, c_B. According to the electrostatic theory model, layer A and layer B can be considered as two infinite charging plates. putting the origin of coordinate x at the interface between two layers, since the charge distributions possess symmetry normal to x-direction, the field strength at point P consists of three parts (Fig. 1), the field strength E_1, E_2 and E_3 are produced by charges in the region of $-c_A O$, OP and Pc_B respectively. The field strength at point P will be

$$E = E_1 - E_2 + E_3 = \frac{\sigma_1(x)}{2\varepsilon_0} - \frac{\sigma_2(x)}{2\varepsilon_0} + \frac{\sigma_3(x)}{2\varepsilon_0}$$

$$= \frac{1}{2\varepsilon_0}\left[\int_{-c_A}^0 \rho_A dx - \int_0^x \rho_B dx + \int_x^{c_B} \rho_B dx\right]$$

$$= \frac{1}{2\varepsilon_0}[\rho_A c_A + \rho_B c_B - 2\rho_B x] \qquad (1)$$

Considering the significant interface, that is $x = 0$, the formula (1) can be simplified as

$$E = \frac{1}{2\varepsilon_0}[\rho_A c_A + \rho_B c_B] \qquad (2)$$

The identical results can be obtained by Gauss law. For 1 mol, the potential energy between unit layers is represented as

$$A = \frac{N_0 \cdot e_t}{2}\left(\int_{-c_A}^0 E dx + \int_0^{c_B} E dx\right)$$

$$= \frac{N_0 \cdot e_t}{4\varepsilon_0}\left[\int_{-c_A}^0 (\rho_A c_A + \rho_B c_B)dx\right.$$

$$\left. + \int_0^{c_B} (\rho_A c_A + \rho_B c_B)dx\right]$$

$$= \frac{N_0 \cdot e_t}{4\varepsilon_0}(\rho_A c_A + \rho_B c_B)(c_A + c_B) \qquad (3)$$

where $N_0 = 6.0221 \times 10^{23} \text{mol}^{-1}$ is the Avogadro's number, $\varepsilon_0 = 8.85 \times 10^{-12} \text{C}^2\text{N}^{-1}\text{m}^{-2}$ is the electromagnetic constant, e_t is the charges included in 1 mol mineral. Formula (3) shows the potential energy of the electrostatic interaction between unit layers in interstratified minerals.
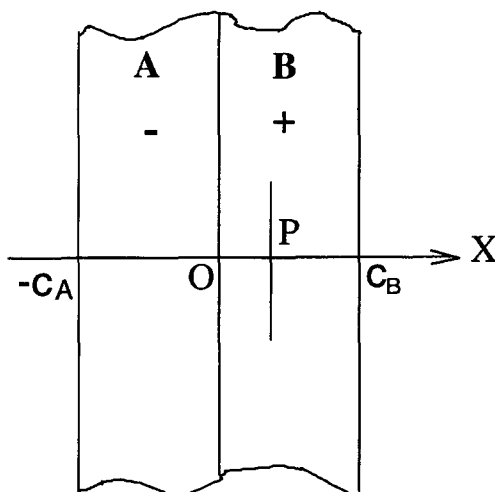

FIG. 1. Schematic structure of interstratified mineral. The X direction corresponds to the stacking direction of unit layers.

Discussion

Let us take the koenenite as an example for practical calculation. In koenenite, the chloride layers negatively charged of composition $Na_{0.65}Mg_{0.35}Cl_2$ alternate along the c axis with the hydroxide layers positively charged of composition $Mg_{0.64}Al_{0.36}(OH)_2$, thus the two components in different classes are coherently interstratified within one crystal (Allmann et $al.$, 1968). Assuming the chemical composition of koenenite is represented by the formula $(Na_AMg_BCl_2) \cdot n[Mg_aAl_b(OH)_2]$, for the ideal composition of koenenite, the chemical formula can be represented as $[Na_{0.65}Mg_{0.35}Cl_2] \cdot 1.78[Mg_{0.64}Al_{0.36}(OH)_2]$. If chloride and hydroxide layers are displayed by A and B, we can get that $e_t =$ nbe, $\rho_A = nbe/V_A$, $\rho_B = nbe/V_B$, $c_A = 1.99$ and $c_B = 3.02$ Å. Here $e = 1.602 \times 10^{-19}$C, is the elementary charge, V_A and V_B are the cell volume of A and B layers, equal to 156.23 and 87.763 Å^3, respectively, n and b come from the chemical formula. For 1 mol koenenite, according to formula (3), we get

$$A = 471.52 \text{ kJmol}^{-1}$$

This result suggests that the potential energy of the electrostatic interaction between chloride and hydroxide layers in koenenite belongs to ionic bond, which is weaker than that in NaCl crystal (the lattice energy is 752 kJmol^{-1}), a typical ionic crystal. This result is also helpful to estimating the mineral-forming conditions and analysing the microstructural defects (Qin and Cao, 1998).

The quantitative calculating method proposed in this note is established based on the model of electrostatic theory and simplification of mineral structure, and it is limited within the interstratified minerals only consisting of two different unit layers in its application. However, as a quantitative method, it would have widespread significance to the crystal structure and chemistry studies of the layer minerals, non-layer minerals, even the organic minerals.

References

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