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NOTE

THE INTERLAYER BONDING IN ONE-LAYER KAOLIN STRUCTURES

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If one calculates the electrostatic energy of one-layer kaolin-type structures as a function of the shift (in two-dimensions) of one layer relative to the next, the resulting potential energy map will have minima which coincide with the known stable structures (Wolfe and Giese, 1972). These are right- and left-handed kaolinite with shifts relative to the pseudohexagonal axes of (0, 2/3) and (2/3, 0) and the shift (1/3, 1/3) which occurs in pseudotwinned kaolinite (Mansfield and Bailey, 1972). These are stackings which produce a close juxtaposition between hydroxyl groups and oxygen anions of adjacent layers and this juxtaposition seems to be a necessary feature for stability (Hendricks, 1938). There are three other geometrically suitable, but not naturally occurring shifts: (0, 0), (2/3, 1/3) and (1/3, 2/3); which are located on or near saddle points in the potential energy map (Wolfe and Giese, 1972). More recent work by Cruz *et al.* (1972) and Giese (1973) has demonstrated that there is an electrostatic attraction between the layers in the kaolin minerals and that the attraction involves long hydrogen bonds (Giese, 1973). As a further test of the validity of our proposal that stable stackings correspond to potential energy minima, we have examined the interlayer bonding in the one-layer kaolin polytypes.

As described elsewhere (Giese, 1973), the existence of an electrostatic attraction between the layers of a phyllosilicate can be demonstrated by numerically computing the slope of the electrostatic energy as a function of interlayer separation. To do this involves computing the energy of the normal mineral and one which has a slightly larger interlayer distance; the slope is the energy difference divided by the increase in separation. The present computations were done following a procedure described elsewhere (Giese, 1973) using the structure of the kaolin layer as determined by Zvyagin (1967) with the hydrogen positions of Datta and Giese (1973).

The results are plotted as a contour map (Fig. 1) in which a line drawn from the origin to any point on the map surface represents the projection of the *c*-axis of the unit cell for that particular interlayer shift. The value of the elevation at any point (as indicated by the contour lines) gives the slope of the electrostatic energy vs interlayer separation for the polytype represented by that particular unit cell. Thus the map gives the value of the slope for all possible one-layer kaolin minerals. Elevations (solid contour lines) are positive slopes and indicate electrostatic attraction between layers while the shaded areas are negative slopes and represent repulsion between layers. The numbers associated with the figure are the stacking codes as given by Newnham (1961).

Figure 1 shows that stackings 7, 13 and 25 have the largest interlayer bonding as indicated by the values of the slope; 0·169, 0·123 and 0·120 $e^2 Å^{-1} Å^{-1}$, respectively. Two of the other three stackings, 1 and 19, have less interlayer bonding, 0·062 and 0·062 $e^2 Å^{-1} Å^{-1}$, and should be less stable while stacking 31 has a small electrostatic repulsion ($-0{\cdot}003\ e^2 Å^{-1} Å^{-1}$) and must be unstable. The interlayer bonding calculations are consistent with but not as clear-cut as the potential energy map (Wolfe and Giese, 1972).

This lack is due to the neglect of the van der Waals and repulsion contributions to the interlayer bonding. The van der Waals attraction between layers is probably very small since the distances between atoms on either side of the interlayer region are large. Bailey and Daniels (1973) estimate that these forces between muscovite layers amount to only 8 per cent of the electrostatic forces. This result and the calculations by Busing (1970) suggest that the repulsion contribution should be larger than the van der Waals term so that the net sum of interlayer forces is zero. The numerical sum of the van der Waals and repulsion terms will be negative (repulsion) which the electrostatic energy (positive) will have to dominate if the stacking is to be stable. Calculating the

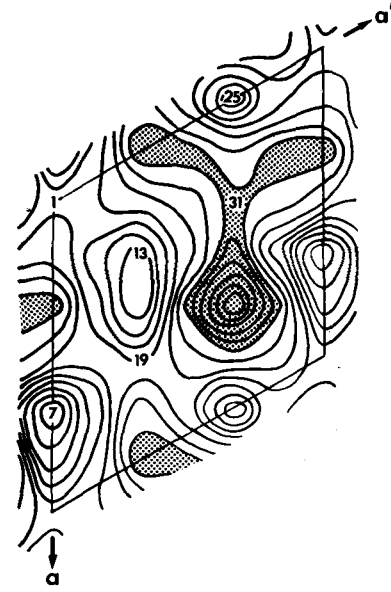


Fig. 1. Contour map of the slope of the electrostatic energy vs interlayer separation distance as a function of the interlayer stacking translations in two-dimensions for one-layer kaolin-type structures. The contour interval is $0{\cdot}020\ e^2 Å^{-1} Å^{-1}$ and negative slopes are shaded. The a and a' axes are the pseudohexagonal unit cell axes.

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electrostatic contribution to the interlayer bonding as approximated here by the slope of the energy vs interlayer separation distance is useful in that a negative value means that the stacking cannot be stable but a small positive value may not be definitive since the magnitudes of the repulsion and van der Waals terms are not known.

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