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## CHOICE OF ORIGIN AND ITS EFFECT ON CALCULATED X-RAY SPACINGS FOR THIN MONTMORILLONITE CRYSTALS

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## ABSTRACT

The nature of the crystal surface, and its influence on the position of diffraction maxima, for small crystals is emphasized.

Clay mineralogists commonly utilize calculations of intensities and spacing of basal (00*l*) reflections of phyllosilicate minerals in order to help interpret diffractograms. The usual relation employed for one-dimensional calculations is

$$I = \Xi |F|^2 \Phi,$$

where  $\Xi$  is the appropriate Lorentz and polarization factor,  $|F|^2$  is the squared modulus of the unit layer structure factor,<sup>1</sup> and  $\Phi$  is a geometrical function which depends only on the number and distribution of unit layers along reciprocal *c*. For normal periodic crystals,  $\Phi$  may be the Laue interference function, and for interstratified materials,  $\Phi$  is most conveniently expressed as the Laue interference function in the form of a Fourier series (James, 1965, p. 522).

The purpose of this report is to indicate that the selection of an origin for a mica structure implies a judgment concerning the termination of the crystals. For thick arrays of unit layers, alternative origins are equivalent, but for thin crystals ( $N < 12$  where  $N$  is the number of unit layers per crystallite) the crystal termination constitutes a boundary condition that can greatly influence calculated positions of (00*l*) maxima. The effect of  $N$  on calculated spacings has been discussed by Ross (1968) and Reynolds (1968), however, neither of these papers stressed the nonequivalence of different centers of symmetry for calculations of this sort.

The calculations presented here consider two origins for ethylene glycol-montmorillonite. The structure proposed by Brindley (1956) and

1 For a centrosymmetric case, the imaginary component disappears and

$$F = \sum n_a f_a \cos(2\pi z_a/d)$$

where  $n_a$  is the number of atoms of type *a* per layer unit cell,  $f_a$  is the scattering power of atoms of type *a*, and  $z_a$  is the distance in Å of type *a* atoms from the origin, and  $d$  is the basal spacing, which is considered to be continuously variable.

Reynolds (1965) is assumed; the unit cell has two centers of symmetry in projection onto reciprocal  $c$ , namely one centered on the octahedral aluminum sheet, and one centered between single glycol layers which constitute the interlamellar complex. Iron substitution, atomic coordinates, and temperature factors are as given by Reynolds (1965); the random powder Lorentz-polarization factor is used in all calculations.

Figure 1 shows the squared moduli of the structure factors for glycol-montmorillonite versus  $2\theta$  for copper  $K\alpha$  radiation. The dashed curve was calculated on the basis of an octahedral origin and the solid curve for an origin centered in the interlamellar region. The positions of montmorillonite (00 $l$ ) maxima are indicated, and it can be seen that, as required by theory, the two  $|F|^2$  curves have identical values at these positions. For very thick crystals the interference function  $\Phi$  has appreciable values only at these reciprocal lattice nodes, hence identical intensities and spacings are obtained by calculations assuming either symmetry center as the origin.

For very thin crystals, however, maxima in the  $\Phi$  function have considerable breadth and the final diffraction profile includes contributions from regions adjacent to the reciprocal lattice nodes. Given the very different forms of the two  $|F|^2$  curves of Figure 1, equivalent diffraction maxima will be displaced non-similarly.

The cause for these differences lies in the definitions implicit in the se-

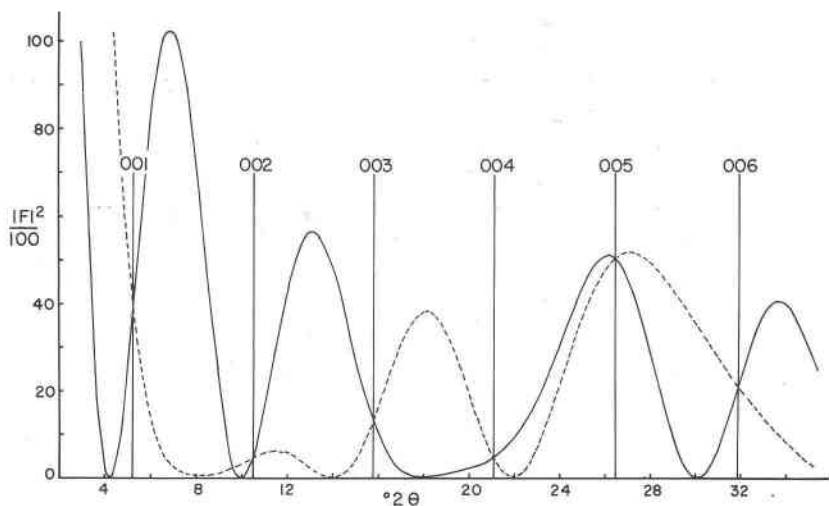


FIG. 1.  $|F|^2$  versus  $2\theta$  (Cu  $K\alpha$  radiation) for ethylene glycol-montmorillonite. Dashed curve was calculated assuming an octahedral origin, and the solid curve is based on an interlayer origin.

lection of a particular symmetry center as the origin. If the interlayer region is selected, the calculation sums atomic scattering vectors up to the center of the octahedral sheet and, by reflection, down to the center of the next octahedral sheet. In short, the crystal is visualized as terminating on a truncated octahedral sheet, a condition that does not appear very realistic. Alternately, if the octahedral sheet is selected as the origin, the crystal surface consists of the basal silicate oxygen plane followed by a monolayer of glycol and the exchangeable cations; this situation corresponds more closely to currently-accepted concepts of clay surfaces.

Figure 2 shows for glycol-montmorillonite ( $d_{001} = 16.86 \text{ \AA}$ ), the calculated apparent spacing of the (001) and (002) maxima as a function of  $N$

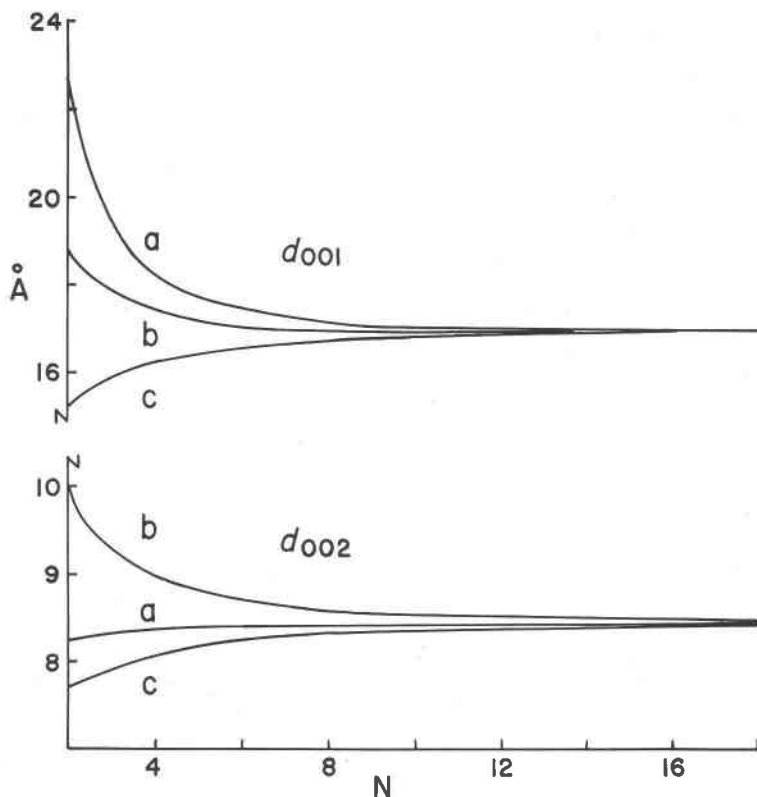


FIG. 2. Apparent spacings of glycol-montmorillonite (001) and (002) maxima as a function of  $N$  for three different models of the crystallite surface.

- a) Octahedral origin, crystal terminates on glycol molecules
- b) Octahedral origin, crystal terminates on basal oxygen atoms
- c) Interlayer origin, crystal terminates on octahedral aluminum atoms

for both of the symmetry-center origins. Curve (a) is based on an octahedral origin, and curve (c) on an interlamellar origin. To illustrate more fully the effect of the crystal surface condition, curve (b) was calculated as for (a), except that glycol was eliminated from the external surfaces, causing the hypothetical crystallite to terminate on a bare silicate oxygen surface. The differences among these models are evident. Curve (c) is regarded as unrealistic, but significant differences can still be seen between calculated results for a bare oxygen surface and for a monolayer of glycol on the surface. The differences are great enough for thin crystallites so that some insight into the surface of montmorillonite could be gained from experimental measurements. We have obtained experimental evidence bearing on this suggestion and these data will be reported separately. These calculations show that a choice of origin is not arbitrary for calculated diffraction profiles from thin crystals. The investigator must choose an origin that is consistent with the nature of the crystallite surfaces.

#### CONCLUSIONS

1. Possible origins such as centers of symmetry for mica-like minerals are not equivalent for calculations of X-ray spacings involving very thin ( $N < 12$ ) crystallites.
2. The choice of a symmetry center as the origin involves an implicit definition of the crystal surface.
3. For montmorillonite, and perhaps other clays, variations in apparent spacings are large (at small values of  $N$ ) among different possible models of the crystallite surface. Hence, information on the nature of the crystal surface could be obtained by appropriate laboratory measurements.

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