

## A TRANSMISSION ELECTRON MICROSCOPY CONTRIBUTION TO THE STRUCTURE OF KAOLINITE

**Key Words**—Crystal structure, Hydrogen positions, Kaolinite, Selected area electron diffraction, Transmission electron microscopy.

The crystal structure of kaolinite is not as well known as that of its two-layer polymorph, dickite, principally because the former does not form sufficiently large and coherent crystals suitable for routine single crystal analytical techniques. The idealized structure of kaolinite was first proposed by Pauling (1930), and the structure was subsequently refined from its X-ray powder diffraction pattern by Brindley and Robinson (1946). The latter authors concluded that the kaolinite structure was triclinic with a single 1:1 (~7 Å) layer. In agreement with an earlier report (Gruner, 1932), they observed no reflections of the type (*hkl*):  $h + k = 2n + 1$ , implying C-face centering for their chosen “pseudo-monoclinic” cell.

Such a C-face centered triclinic cell, however, is not found in the International Tables of Crystallography, because the triclinic axes of such a cell can always be changed to give a cell of half the volume with no C-face centering required. The cell axes could be redefined as

$$\begin{aligned}a' &= \frac{1}{2}(a - b), \\b' &= \frac{1}{2}(a + b), \text{ and} \\c' &= c \text{ (see Figure 1).}\end{aligned}$$

The cell parameters of Suitch and Young (1983) give  $a' = 5.153$ ,  $b' = 5.167$ ,  $c' = 7.403$  Å,  $\alpha' = 107.870^\circ$ ,  $\beta' = 95.890^\circ$ ,  $\gamma' = 120.085^\circ$ . The basal plane is thus clearly pseudohexagonal. Heretofore, the C-face centered cell has been chosen principally to allow ready comparison of the kaolinite and dickite structures.

Later structural investigations using texture electron diffraction (Zvyagin, 1960), X-ray diffraction of a single crystal (Drits and Kashaev, 1960), and Rietveld refinement of the hydrogen atom positions using neutron powder diffraction data (Adams, 1983) have all assumed C-face centering of the “pseudo-monoclinic” cell.

In contrast to these authors, Suitch and Young (1983), in their Rietveld refinement of kaolinite using both X-ray and neutron powder diffraction data, released this positional constraint. They concluded from their X-ray refinement that, within experimental error, the non-hydrogen atom positions were consistent with C-face centered *P*1. In their neutron powder profile refinement of the hydrogen and O(H) atoms they fixed the remaining 18 non-hydrogen atoms at their X-ray refined non-centered positions. They concluded from

this refinement that the positions of the inner-hydroxyl hydrogen atoms destroyed the C-face centering. If these authors had fixed the non-hydrogen atom positions to be C-face centered, as observed by previous authors and implied by their own X-ray results, a significantly different result might have been obtained. This conclusion is reinforced if the relative contributions of non-hydrogen and hydrogen atoms to neutron diffraction intensities are considered. From the derived models of Suitch and Young (1983), labeled AHR and GDR, the contribution of non-hydrogen atoms to the intensities of reflections (*hkl*):  $h + k = 2n + 1$  is significantly greater than that of the hydrogen atoms. In other words, the result of the neutron powder diffraction profile refinement was heavily weighted by the positions assumed for the non-hydrogen atoms in the starting model. Therefore, serious doubt can be raised about their refined hydrogen atom positions and their subsequent conclusion that the two inner-hydroxyl O–H bonds in kaolinite are differently oriented.

The question still remains, are the atom positions in each half of the “pseudo-monoclinic” cell related by C-face centering? Transmission electron microscopy (TEM) is able to answer this question for both non-hydrogen and, to some extent, hydrogen atom positions.

A major difference between X-ray and electron diffraction is the much greater strength of interaction with crystalline substances in the latter. The strength of this interaction, in fact, is such that multiple scattering effects generally become important for crystal thicknesses,  $\geq 100$  Å. Thus, even kinematically very weak reflections rapidly build up significant intensity as a function of crystal thickness with electron diffraction.

The commonly observed selected area electron diffraction (SAD) pattern down the [001] zone axis for kaolinite (Figure 2) indicates that the condition (*hkl*):  $h + k = 2n$  holds. Typical crystal thicknesses, observed via high-resolution transmission electron microscopy (HRTEM), for this kaolinite specimen (kaolinite #2 described by Thompson and Cuff, 1985) were 300–400 Å. Multislice calculations (see, for example, Anstis, 1977) of the expected [001] zone axis intensities for a range of crystal thicknesses (7 to 716 Å, i.e., 1 to 100 unit cells) were made. Two structural models were chosen for these calculations. The first model used the

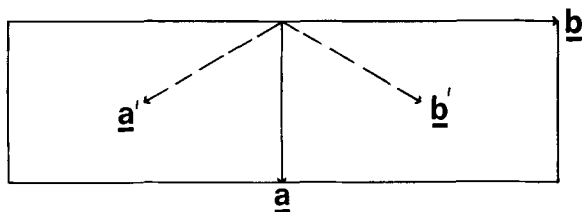


Figure 1. Diagram showing that for a C-face centered triclinic cell the axes can always be redefined as shown for the kaolinite cell reported by Suitch and Young (1983):  $a' = \frac{1}{2}(a - b)$ ,  $b' = \frac{1}{2}(a + b)$ . Note that  $\gamma'$ , the angle between  $a'$  and  $b'$ , is  $120.085^\circ$ .

refined atomic positions AHR reported by Suitch and Young (1983), in which all atoms are non-centered. The second model was based on the Suitch and Young model, AHR, but non-hydrogen atoms were placed in averaged C-face centered positions. Both calculations gave significant intensity for reflections excluded by C-face centering. The calculated electron diffraction intensities for a kaolinite crystal of average thickness (358 Å) derived for the two models are listed in Table 1.

In Model 1 where all atoms are non-centered, as reported by Suitch and Young (1983), the calculated intensities clearly disagree with the observed intensities. In Model 2, where only hydrogen atoms are non-centered, the disagreement is less certain. Therefore, the non-hydrogen atoms in kaolinite are probably C-face centered. Moreover, no sound evidence demonstrating that the hydrogen atoms in kaolinite are not C-face centered has appeared. Furthermore, because the non-hydrogen atoms are centered, there is no obvious cause for the non-centering of the hydrogen atoms.

Table 1. Electron diffraction intensities from multislice calculations for kaolinite.

hkl	$I_{\text{calculated}}$	
	Model 1	Model 2
010	324	4
100	1322	1
020	1698	1878
110	10,000	10,000
110	8102	8510
120	103	11
120	1	9
030	5	1
130	227	206
130	68	18
200	1532	2477

Model 1 used refined atomic parameters AHR from Suitch and Young (1983). Model 2 is the same as Model 1, except non-hydrogen atoms are placed in averaged C-face-centered positions. Multislice calculations based on 50 slices (~358 Å) and 100 keV.

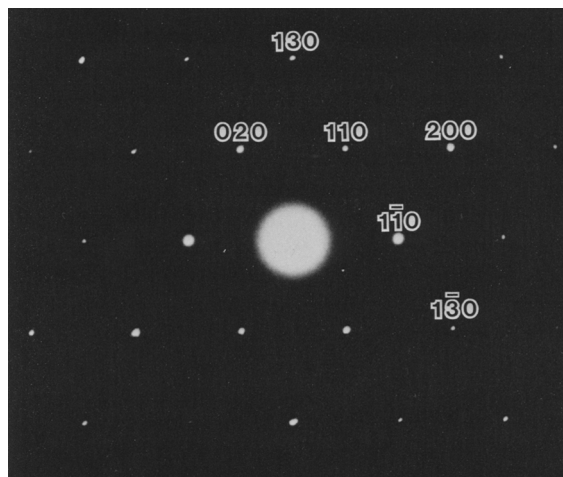


Figure 2. Selected area electron diffraction pattern down the [001] zone axis of kaolinite. The reflections are labeled in terms of the C-face-centered triclinic cell. Note the total absence of reflections ( $hk0$ ):  $h + k = 2n + 1$ .

The conclusions of Suitch and Young (1983) regarding the hydrogen atom positions and hydrogen-bond lengths in kaolinite must be treated with caution given their choice of starting model prior to neutron powder profile refinement and the electron diffraction results here presented. All evidence to date requires that the "pseudo-monoclinic" cell of kaolinite is C-face centered for the non-hydrogen atoms. Future powder profile refinements would do well to include this constraint to reduce the number, and thereby improve the reliability, of atomic positions. The question as to whether the hydrogen atom positions are centered or not is yet to be resolved conclusively.

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