

THE INFLUENCE OF CRYSTALLITE SIZE ON THE APPARENT BASAL SPACINGS OF KAOLINITE

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Abstract—For very small crystallites diffraction theory shows not only broadening of powder lines, but generally also a shift of the line position, depending on the change of the structure factor over the range of broadening. For decreasing thickness of kaolinite crystals (less than 50 layers) an increasing shift of reflections is found: the lines (001), (002), (004) and (006) are shifted to apparently larger spacings, the lines (003) and (005) to smaller spacings, resulting in a nonintegral series. Presuming a known crystallite size, tables are given for evaluating true spacings from measured values of 2θ .

INTRODUCTION AND THEORETICAL BACKGROUND

It is well known that crystals of very small size show a considerable broadening of their X-ray reflections, and it has been frequently reported that broadened lines are shifted to unexpected 2θ -positions. Especially in clay mineralogy, where small crystallite size is common, a range of basal spacings is quite usual. Reynolds (1968) and Ross (1968) were the first authors to calculate reflection shifts depending on crystallite size: Reynolds for illite, Ross for biotite, muscovite, montmorillonite, mixed-layer clays, graphite and periclase. Tettenhorst and Roberson (1973) give results for glycol-montmorillonite.

This paper evaluates the effects of finite crystallite size on kaolinite basal reflections. In a recent investigation (Trunz, 1974) the author studied the line profiles of the basal reflections of kaolinite. As it turned out, even in "well crystallized" samples the domains of crystal perfection (i.e. crystallites) are smaller than 20 or 30 layers, which made these calculations necessary.

Neglecting geometrical and other factors the intensity distribution in reciprocal space is given by

$$I = |F|^2 \cdot S^2 \tag{1}$$

where $|F|^2$ is the structure factor and S is the interference function

$$S = \frac{\sin NH\pi}{\sin H\pi} \tag{2}$$

H is a point in reciprocal space, given in terms of the Laue indices (hkl), which are not necessarily integers. N is the number of unit cells in the directions of a , b and c , respectively. Though recently Güven (1974a, 1974b) has given a detailed discussion of the function, it seems necessary to repeat some of its main properties. First the function is perfectly symmetrical with respect to the reciprocal lattice point. Secondly it has a main maximum around the reciprocal lattice

point within the range

$$H = \pm \frac{1}{N} \tag{3}$$

and smaller subsidiary maxima beyond it. Hence the breadth of the main maximum is inversely proportional to the number of unit cells. Within the range of (3) the structure factor will in general be asymmetric with respect to the reciprocal lattice point and will show a continuous and curved slope. Of course, $|F|^2$ has to be calculated not only for $H = \text{integer}$, but for all non-integral H .

For a finite number of unit cells the intensity distribution (1) will be no longer symmetrical with respect to the reciprocal lattice point. Thus a shift of the peak or any other measure of position is caused, which is proportional to $\delta|F|^2/\delta H$ and to the breadth of the main maximum.

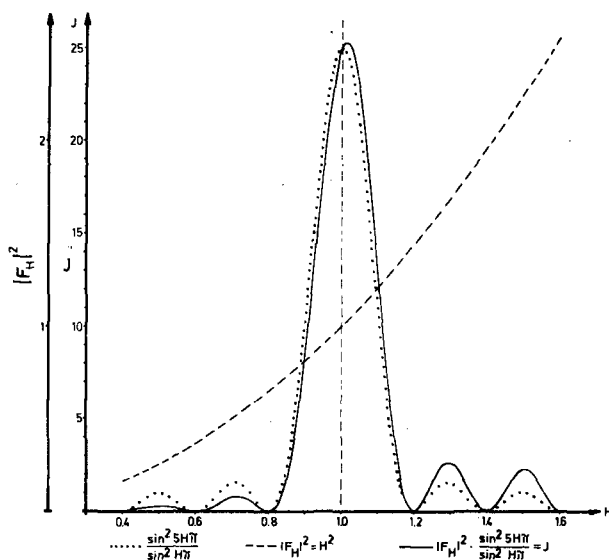


Fig. 1. Theoretical line-profile for 5 unit-cells. The interference function is given by the dotted line, and the arbitrary structure-factor-function by the dashed line. The solid line then shows the theoretical line-profile.

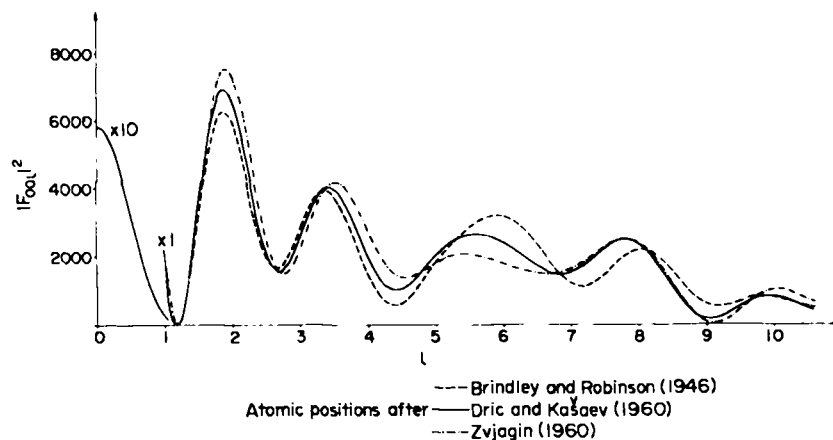


Fig. 2. Structure-factor-function for the basal interferences of kaolinite, as resulting from different structure determinations.

The observed lattice spacing is then only an apparent one which is smaller or larger than the actual spacing. Thus irrational relations of $d_{(hkl)}/nd_{n(hkl)}$ are caused, which usually are a characteristic of a variable lattice constant.

Figure 1 gives a simple example. The dotted line shows the one dimensional interference function around $H = 1$ for a crystal of $N = 5$ unit cells. The peak height is $N^2 = 25$. This profile has to be multiplied with $|F|^2$, which for simplicity is assumed to be equal to H^2 in this case (dashed line). The resulting profile is then given by the solid line: the peak position is found to be shifted to $H = 1.01$ and the resulting observed spacing is $d_{obs} = d_{true} \cdot 1/1.01$.

Figure 1 also shows a considerable change in intensities of the subsidiary maxima. It is easily understood that a distribution of crystallite sizes will finally lead to an assymmetrically tailed out powder line.

APPLICATION TO THE BASAL SPACINGS OF KAOLINITE

For this one dimensional case, (1) simplifies to

$$I_{(001)} = |F_{00l}|^2 \cdot \frac{\sin^2 Nl\pi}{\sin^2 l\pi}$$

Though each reflection has a three dimensional intensity distribution in reciprocal space, this simplification is justified. The large crystallite size in the a - b -plane makes any contributions from these directions negligible.

For the atomic z -positions three different structure determinations are available from the literature. These are, Brindley and Robinson (1946), Zvjagin (1960) and Dric and Kašev (1960). The scattering factors for the ionization states Al^{3+} , Si^{4+} and O^{1-} were those of Cromer and Mann (1968). The resulting $|F|^2$ functions are shown in Fig. 2. They look rather similar and lead, with the exceptions of $l = 7$ and $l = 9$, to practically the same results in line shifts. The largest slope is found around $l = 1$, leading to a shift of the (001) line greater than that of all other lines. A decrease of $|F|^2$ and thus a shift to smaller l (= larger spacings) is found for $l = 1, 2, 4, 6$; positive rise and a shift to greater l (= smaller spacings) for $l = 3$ and $l = 5$. Within the range of equation (3), I_{00l} was calculated for the three sets of atomic positions and crystals of 5–50 layers. With the centroid chosen as measure of line position, the mean and standard deviation of l_c is given in Table 1. The

Table 1. Centroid positions and standard deviation (in parentheses) in terms of Laue-index l_c for crystals of 5–50 layers

| Number of layers | l_c | | | | | |
|------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| 5 | 0.955 (1) | 1.996 (1) | 3.009 (1) | 3.990 (3) | 5.005 (2) | 5.999 (1) |
| 6 | 0.968 (1) | 1.997 (1) | 3.006 (1) | 3.993 (2) | 5.003 (2) | 5.999 (1) |
| 7 | 0.976 (1) | 1.998 (1) | 3.005 (1) | 3.995 (2) | 5.003 (1) | 5.999 (0) |
| 8 | 0.981 (1) | 1.999 (1) | 3.004 (1) | 3.996 (1) | 5.002 (1) | 5.999 |
| 9 | 0.985 (1) | 1.999 (0) | 3.003 (0) | 3.997 (1) | 5.002 (1) | 5.999 |
| 10 | 0.988 (0) | 1.999 | 3.002 | 3.997 (1) | 5.001 (0) | 6.000 |
| 12 | 0.992 | 1.999 | 3.002 | 3.998 (1) | 5.001 | 6.000 |
| 14 | 0.994 | 2.000 | 3.001 | 3.999 (1) | 5.001 | 6.000 |
| 16 | 0.995 | 2.000 | 3.001 | 3.999 (0) | 5.001 | 6.000 |
| 18 | 0.996 | 2.000 | 3.001 | 3.999 | 5.000 | 6.000 |
| 20 | 0.997 | 2.000 | 3.001 | 3.999 | 5.000 | 6.000 |
| 25 | 0.998 | 2.000 | 3.000 | 4.000 | 5.000 | 6.000 |
| 30 | 0.999 | 2.000 | 3.000 | 4.000 | 5.000 | 6.000 |
| 40 | 0.999 | 2.000 | 3.000 | 4.000 | 5.000 | 6.000 |
| 50 | 1.000 | 2.000 | 3.000 | 4.000 | 5.000 | 6.000 |

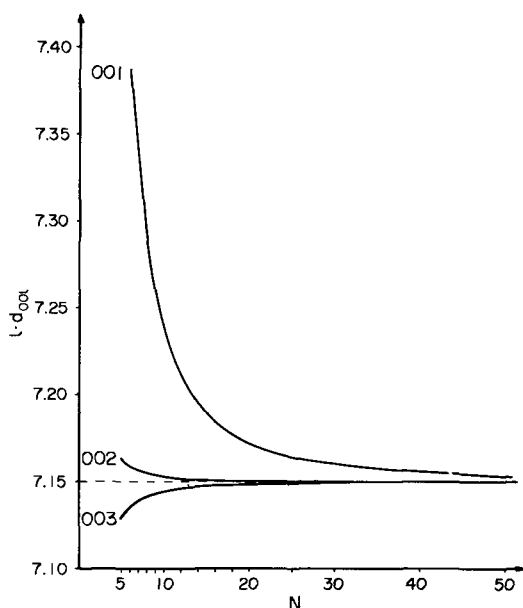


Fig. 3. Dependence of apparent basal spacings of kaolinite on the number of layers in a crystallite.

seventh and higher orders were omitted, as the error exceeded the shift. The true basal spacing is then found by inserting l_c , centroid position of 2θ and centroid wavelength (Taylor *et al.*, 1964) in the Bragg equation.

If the actual spacing is taken to be 7.15 Å, Table 1 converts to Figs. 3 and 4. As will be shown, a true spacing of 7.10 or 7.20 Å may be taken as well without introducing a significant error. For that reason Table 1 is free of any major errors.

PRACTICAL CONSIDERATIONS

Though the center of gravity is somewhat tedious to determine it has some theoretical and practical advantage over the peak position. In powder diffractometry instrumental aberrations are extremely large at low angles, giving an additional line shift of several hundredths of a degree 2θ towards lower angles. For example with $\text{CuK}\alpha$ radiation and a standard diffractometer setting the corrected centroid gives an angle about 0.06° 2θ higher than the observed peak position. The error is then about 0.04 Å. According to the formulas collected by Wilson (1963) accurate corrections can be applied to the centroid, but not to the peak position.

The calculated centroid is a function of the range involved. Thus when using centroids in the Bragg or any other equation, comparable ranges of $\Delta 2\theta$, $\Delta \lambda$ on a wavelength scale or Δs in reciprocal space have to be used. Formulas to convert these from one to another are given by Edwards and Langford (1971). In practice a certain misfit of ranges may occur, i.e. those of $\Delta 2\theta$ and $\Delta \lambda$ will exceed that of equation (3). In such cases the corrections applied from this paper are minimum corrections.

CONSIDERATION OF POSSIBLE ERRORS

Though the accuracy of the presented results is limited mainly by the accuracy of the structure determinations, there are two possible sources of minor errors. The first one is the true basal spacing (if differing from 7.15 Å) which influences the results via $\sin \theta/\lambda$ dependence of the atomic scattering factors, or the use of improper scattering factors by more ideal than realistic ionization states.

A test calculation for 7.10 Å showed practically no effect and only a drastic change in ionization states to neutral atoms gave an additional effect of $\Delta l = -2 \times 10^{-3}$ for the worst case of (001) and 5 layers.

The second source of error results from neglecting the temperature factor. An overall factor of $B = 4 \text{ \AA}^{-2}$ and again the worst case of (001) and 5 layers leads to $\Delta l = -2 \times 10^{-4}$ and is thus negligible, too.

CONCLUSIONS

Especially in clay mineralogy the effect of crystallite size on apparent spacings is quite common. Though for kaolinite this effect is small if compared to mica minerals, it should yet be considered if a reasonable accuracy of lattice constants is required.

When, at a first glance, a nonintegral series of spacings is found, the data should be compared for the curves of Figs. 3 and 4. In some cases they may reduce to a single spacing and give an estimation of the mean thickness of crystallites. If this fails, it is an indication of some type of disorder involving a variable layer-spacing.

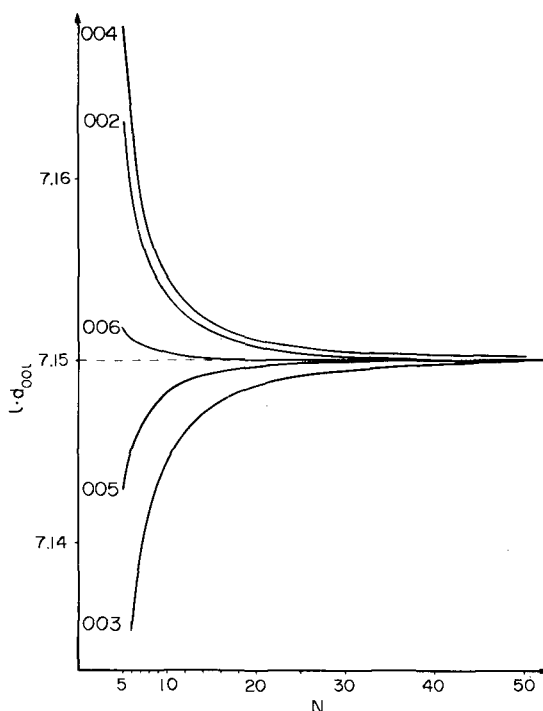


Fig. 4. Dependence of apparent basal spacings of kaolinite on the number of layers in a crystallite.

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