GURSKAYA, G. V. (1968). *The Molecular Structure of Aminoacids*. New York: Consultants Bureau.

HAUPTMAN, H. & KARLE, J. (1956). *Acta Cryst.* **9**, 45.

International Tables for X-ray Crystallography (1962). Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP, A Fortran Thermal Ellipsoïd Plot Program for Crystal Structure Illustrations*. ORNL-3794, Oak Ridge National Laboratory, Tennessee.

LAKSHMINARAYANAN, A. V., SASISEKHARAN, V. & RAMACHANDRAN, G. N. (1967). *Conformation of Biopolymers*, Vol. 1, p. 61. London, New York: Academic Press.

SRINIVASAN, R. (1959). *Proc. Indian Acad. Sci.* A**49**, 340, A**50**, 19.

Tables of Interatomic Distances and Configuration in Molecules and Ions (1965). London: The Chemical Society.

WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 152.

X-ray Diffraction Studies on the Transformation of Kaolinite into Metakaolin.
II. Study of layer shift

BY G. B. MITRA AND S. BHATTACHERJEE

Department of Physics, Indian Institute of Technology, Kharagpur, India

The shift of kaolin layers with respect to adjacent layers at different stages of dehydration has been investigated by X-ray diffraction studies of the 020 reflexion of kaolinite. The proportion of planes affected by the defect has been studied quantitatively at different stages of dehydration by a single-line technique similar to that developed by Mitra & Bhattacherjee (1969a). A method for separating two partially overlapped lines has also been developed and applied to recover the 020 line which was found to overlap the $1\bar{1}0$ line. It is concluded that the probability of layer shift increases with dehydration and the crystallite can withstand a relatively larger proportion of planes affected by interlayer variation than by layer shift defects. The defect becomes maximum at about 400°C leading to the collapse of the kaolinite structure and the formation of metakaolin.

Introduction

The dehydration transformation of kaolinite into metakaolin is a subject of immense interest and various authors, *e.g.* Brindley & Nakahira (1959), Johns (1953) and Mitra (1963), have offered different explanations of the transformation process. Mitra (1963) has shown that kaolinite is subject to two specific types of structural defect:

I. Variability of the interlayer spacings.

II. Shifting of the kaolin layers with respect to adjacent layers by $\frac{1}{3}b$ or $\frac{2}{3}b$.

Mitra (1963) described methods of quantitatively evaluating the extent and the probability of these defects in kaolinite and on the basis of his measurements suggested that these defects were likely to be transmitted to and influence the structural changes during dehydration leading to the formation of metakaolin.

Acting on this suggestion, Mitra & Bhattacherjee (1969a, b) have studied the extent of the defects of type I mentioned above and the proportion of planes subject to such defects and have arrived at conclusions regarding the structural changes accompanying the dehydration transformation of kaolinite into metakaolin. The above work constitutes part I of the investigation and the present work, part II. The present work aims at studying quantitatively the defects of type II mentioned above during the dehydration transformation. The objective is the same as in part I; *viz*, to understand the structural changes taking place during the transformation.

Experimental details and observations

As in the case of part I (Mitra & Bhattacherjee, 1969b) a powdered sample of kaolinite from Georgia, U.S.A., was selected for the present work. The average chemical composition of the sample has already been reported in part I. The powdered sample was dehydrated exactly in the way described.

For studying the defects of type II, it was necessary as shown by Mitra (1963) to obtain pure diffraction line profiles of reflexions from planes $hk0$ ($k \neq 3n$, n being an integer). The X-ray diffraction technique for obtaining the line profiles is the same as described by Mitra & Bhattacherjee (1969b). The various reflexions were recorded by a fixed count technique using a Norelco X-ray diffractometer fitted with a Geiger–Müller tube connected to a decade counter so that the overall accuracy of measurement of the intensity was of the order of 1%. It was observed that most of the line profiles of reflexions from planes $hk0$ ($k \neq 3n$) were

either submerged in broad bands of numerous partially overlapping profiles or were too diffuse and weak to be measured with an accuracy consistent with that demanded by the requirements of proper interpretatation. The only lines which could be measured accurately were the 020 and 1$\bar{1}$0 reflexions, which were partially overlapped.

For obtaining the proper level of background scattering, the composite line was considered to be a single line and the method due to Mitra & Misra (1966) was applied. Once the proper background was fixed, the tails of the composite profile could be traced to the points where they merged with the background on either side of the profile. Next, these two partially overlapped profiles were recovered by the method described in the Appendix.

At this stage a deconvolution technique similar to that described by Mitra (1963) was applied to recover the pure diffraction profiles for the two reflexions. This was done for the untreated kaolinite as well as for all the dehydration stages, namely 200, 300 and 400°C. The study was not carried out at dehydration stages above 400°C because at these stages these lines disappear into a weak incoherent scattering. It was observed by the method described in the Appendix, that both these lines were symmetrical at all the dehydration stages and this demonstrated that the reflexions were influenced only by defects of type II and not by any other kind of defect (Mitra, 1963). The probability, α, of a layer shift taking place was determined from these line profiles by the method described below.

Single reflexion method for evaluating α

The intensity profiles for both the 1$\bar{1}$0 and 020 reflexions are results of a convolution of particle size profiles with the profiles characteristic of the particular type of disorder discussed above. Usual methods of deconvolution depend on multiple reflexion techniques similar to that due to Averbach & Warren (1949). In the present case, however, reflexions of higher order for both these were either merged with the reflexions into a near uniform band or too weak to be measured accurately. Hence a single line technique had to be developed.

The present method of determining α is very similar to the method described by Mitra & Bhattacherjee (1969a, b) for the determination of g, the fractional change in the interlayer distance, and γ, the proportion of planes affected by such disorder, in kaolinite.

The defect line profile for defects consisting of layer shifts of type II has been derived by Wilson (1962) and is given by

$$I(\omega) = \frac{12NF^2\alpha}{9\alpha^2 + (4\pi\omega)^2},\qquad(1)$$

where the intensity $I(\omega)$ is measured at a point in reciprocal space distant ω from a reciprocal lattice point l units away from the origin of the reciprocal lattice. ω and l are expressed in units of $2d\sin\theta/\lambda$ where d is the lattice spacing corresponding to the reflexion under study, θ, the semi-angle of deviation and λ the wavelength of radiation used. α is the probability of transition of a normal layer into a shifted layer, F is the structure amplitude of a layer for the given reflexion and N is the number of layers in a particle. The reciprocal point corresponds to $\omega = 0$. The tth order Fourier transform $H(t)$ of the intensity profile $I(\omega)$ is given by (Mitra, 1963)

$$H(t) = NF^2 \exp\left(-\tfrac{3}{2}\alpha t\right).\qquad(2)$$

Again $H(t)$ is given by

$$H(t) = J(t) - iK(t)\qquad(3)$$

where $J(t)$ and $K(t)$ are the real and imaginary parts of the tth order Fourier transform of the line profile. In the present case it is evident from equation (2) that $K(t) = 0$. Hence

$$H(t) = J(t) = NF^2 \exp\left(-\tfrac{3}{2}\alpha t\right).\qquad(4)$$

Then proceeding exactly in the same way as in Mitra & Bhattacherjee (1969a, b) one can arrive at

$$W_D = \frac{3}{16\pi^2}\,[4S\alpha - 3\alpha^2],\qquad(5)$$

where W_D is the variance of the defect profile measured in the angular range S of the line profile. The total variance W of the pure diffraction profile can now be written as

$$W = W_D + W_P\qquad(6)$$

where W_P is the variance of the line profile due to particle size.

Expressing W in 2θ unit and rearranging terms according to Mitra (1964) one obtains the relation

$$\frac{W\cos\theta}{\lambda S} = \frac{1}{\pi^2 P'} - \frac{9\alpha^2}{16\pi^2 d^2}\cdot\frac{\lambda}{S\cos\theta}\qquad(7)$$

where $1/P' = 1/P + \tfrac{3}{4}\alpha/d$; P is the particle size, and d the interplanar distance in the given direction. From the slope of the linear plot of $W\cos\theta/\lambda S$ against $\lambda/S\cos\theta$, α can be determined.

Fig. 1(a), (b) and (c) show $W\cos\theta/\lambda S$ against $\lambda/S\cos\theta$ for samples of kaolinite untreated as well as treated at 200, 300 and 400°C respectively, corresponding to the 020 reflexion. Fig. 3(a) shows that the tails of the intensity distribution corresponding to the 1$\bar{1}$0 reflexion terminate abruptly on the background. For such profiles, the method described above is not suitable since it is not possible to vary S consistently with the conditions for derivation of equation (5) (Wilson, 1962). Hence α was derived only from the (020) reflexion in each case. Values of α are shown in Table 1.

Table 1. *Values of α at different stages of dehydration*
as calculated from the (020) reflexion

Temperature	
30°C	0·014
200	0·016
300	0·021
400	0·023

Results and discussion

Table 1 shows that α increases with dehydration from 0·014 at 30°C to 0·016 at 200°C. Then again α increases from 0·021 at 300°C to 0·023 at 400°C. Since differences between 0·014 and 0·016 and also between 0·021 and 0·023 are rather small it can safely be con-
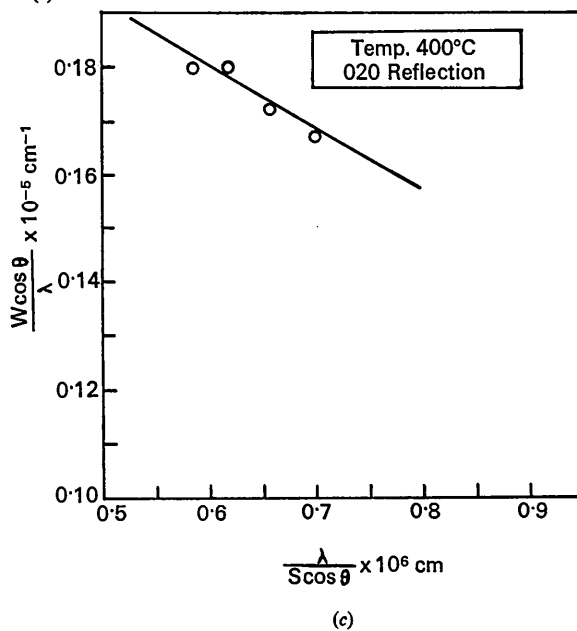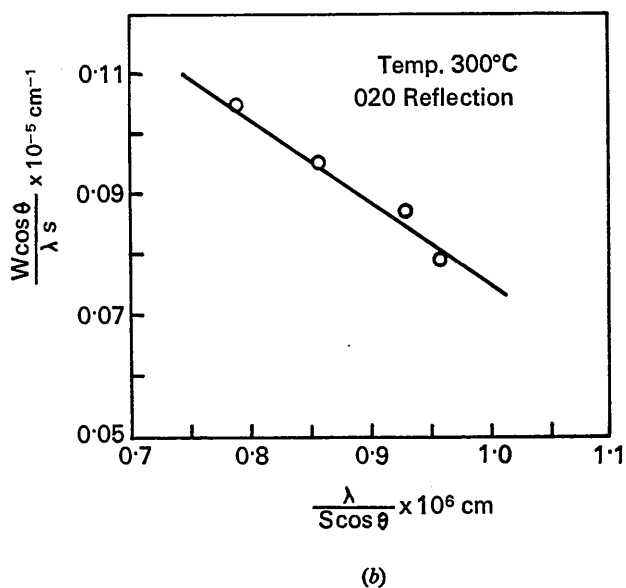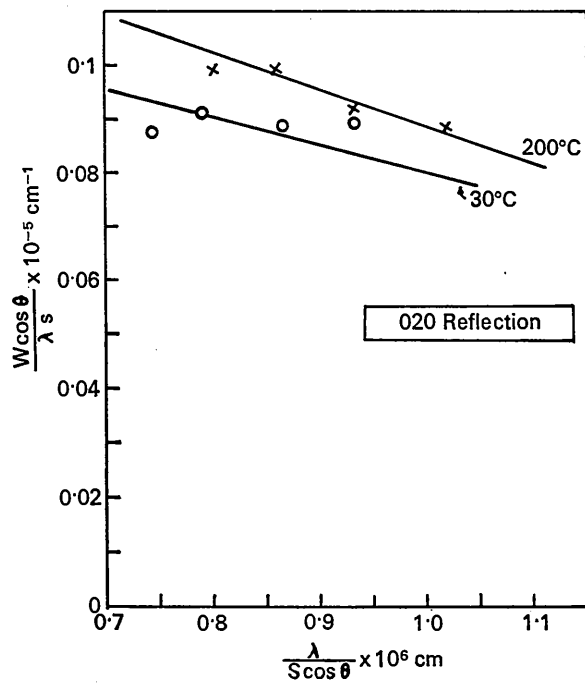

Fig. 1. Graph of $W\cos\theta/\lambda s$ against $\lambda/s \cos\theta$ for samples of koalinite treated at (*a*) 30, 200°C; (*b*) 300°C; (*c*) 400°C corresponding to 020 reflexion.

cluded that the increase takes place in two steps. At the first stage of dehydration the disorder increases by a small amount, *i.e.* the proportion of planes affected by the disorder increases very slightly. Only a few planes at this relatively low temperature are affected. At the second stage (*i.e.* 300°C and above) there is a larger increase in the number of planes affected by the disorder and the number of planes so affected remains nearly unchanged even at 400°C. The enhanced rate of reaction between 200°C and 300°C corresponds to the small endothermic peak in this region in the DTA curve observed by Mitra & Bhattacherjee (1969*b*). On further increase of temperature the layers can sustain no further strain of this type and the structure starts collapsing.

It has been shown in part I that as many as 8% of the planes may be affected by defects of type I, while in the present case the proportion of planes subject to defects of type II does not exceed 2·3%, beyond which value the structure begins to collapse. Hence, it may be concluded that a larger proportion of planes in the lattice can withstand defects of type I than those of type II. The increase in interlayer variation causes a longitudinal strain along the c direction whereas a layer shift of type II will cause a shear in the (100) direction. Hence it is observed that a larger proportion of kaolinite planes can withstand longitudinal strain normal to the kaolin layers than the shear in the (100) plane. Evidently this critical value of the average strain in the two cases preceding collapse of the kaolin layer will be dependent on the average bond force in the two directions and will presumably be different.

It is also abundantly clear that the same particle need not be subject to the two types of defects simultaneously. For example, at 300°C, 8% of planes are subject to defect of type I while only 2·1% to defects of type II. Thus, there is bound to be a large proportion of planes subject to defects of type I while being free from those of type II. There appears to be no reason why there cannot be particles subject to defects of type II which are at the same time free from those of type I. However, it is interesting to note that just prior to collapse of kaolin layers the proportions of planes subject to the two types of defects become nearly equal, about 2·3%. It may very well be that, at this stage, both types of defect are present in a crystallite to such extents that the initial values of strains of the two types are exceeded causing collapse of the kaolin layers in the affected crystallites. The resulting disorder
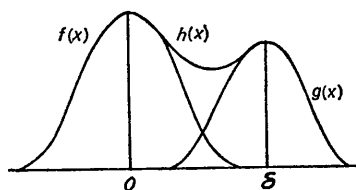
now spreads from crystallite to crystallite affecting the atomic arrangements in the layers more than the layer sequences. This is the reason why while the 002 reflexion is observed even at 600°C (Mitra & Bhattacherjee, 1969*b*), the 020 reflexion vanishes above 400°C. The spreading disorder causes the formation of metakaolin.

APPENDIX

Separation of two partially overlapped lines

Let two X-ray diffraction line profiles $f(x)$ and $g(x)$ about their origins be overlapped to give rise to a combined line $h(x)$ as shown in Fig. 2. The peak positions and the integrated intensities of the two lines are supposed to be known. Let the angular separation between the two lines be δ and let the zero of $h(x)$ coincide with the zero of $f(x)$. Hence

$$h(x)=f(x)+g(x-\delta) . \tag{1}$$

Then

$$\int_{-\infty}^{+\infty} xh(x)\mathrm{d}x=\int_{-\infty}^{+\infty} xf(x)\mathrm{d}x+\int_{-\infty}^{+\infty}(x-\delta)g(x-\delta)\mathrm{d}(x-\delta)$$
$$+\delta\int_{-\infty}^{+\infty} g(x-\delta)\mathrm{d}(x-\delta) . \tag{2}$$

Let
$$\frac{\displaystyle\int_{-\infty}^{+\infty} xf(x)\mathrm{d}x}{\displaystyle\int_{-\infty}^{+\infty} f(x)\mathrm{d}x}=\alpha \quad \text{and} \quad \frac{\displaystyle\int_{-\infty}^{+\infty} xg(x)\mathrm{d}x}{\displaystyle\int_{-\infty}^{+\infty} g(x)\mathrm{d}x}=\beta .$$

Then $S=\displaystyle\int_{-\infty}^{+\infty} xh(x)\mathrm{d}x$ will be given by

$$S=\alpha A+\beta B+\delta B , \tag{3}$$

where $\displaystyle\int_{-\infty}^{+\infty} f(x)\mathrm{d}x=A$ and $\displaystyle\int_{-\infty}^{+\infty} g(x)\mathrm{d}x=B$ are the integrated intensities. Then

$$\frac{S}{A} =\alpha+\beta\,\frac{B}{A} +\delta\,\frac{B}{A} \tag{4}$$

and
$$\frac{S}{B} =\alpha\,\frac{A}{B} +\beta+\delta . \tag{5}$$

By solving (4) and (5) α and β can be evaluated. This treatment can be extended to any number of overlapped lines.

When both α and β are zero, $f(x)$ and $g(x)$ can be separated. This is true only for two overlapped lines. From equation (1) it is obvious that

$$g(x)=h(x+\delta)-f(x+\delta) . \tag{6}$$

Hence
$$h(-x)=f(-x)+g(-x-\delta)=f(x)+g(x+\delta) ,$$

since $g(x)$ and $f(x)$ are both symmetrical, α and β being zero. Or

Fig. 2. Composite profile $h(x)$ formed by partial overlapping of profiles $g(x)$ and $f(x)$.
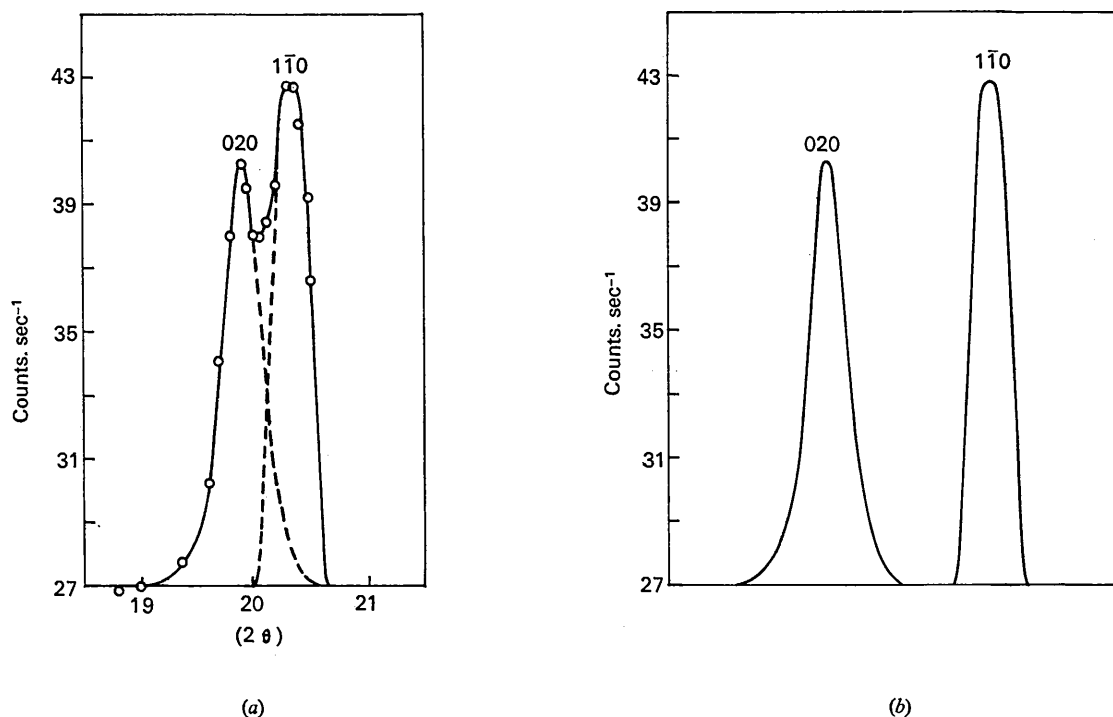
Fig. 3. (a) Experimental composite line profile of kaolinite formed by overlapping of (020) and (1Ī0) line profiles. Dotted lines show the two separate profiles. (b) (020) and (1Ī0) line profiles shown separately after recovering them from (a).

$$h(-x-\delta) = f(-x-\delta) + g(-x-2\delta)$$
$$= f(x+\delta) + g(x+2\delta) . \qquad (7)$$

Combining equations (6) and (7) and repeating the operations mentioned above we have

$$g(x) = h(x+\delta) - h(-x-\delta) + h(x+3\delta)$$
$$- h(-x-3\delta) - g(x+4\delta) , \qquad (8)$$

where $g(x+4\delta)$ can be considered to be zero.

Proceeding in the same way it can be proved that

$$f(x) = h(x) - h(2\delta-x) + h(x-2\delta)$$
$$- h(4\delta-x) + f(4\delta-x) , \qquad (9)$$

where $f(4\delta-x)$ may reasonably be considered to be zero. Equations (8) and (9) can easily be expanded into further terms containing $g(x+n\delta)$ or $f(n\delta-x)$ for proper values of n as the case under consideration may require.

The above method has been used in separating the profiles for the (020) and (1Ī0) lines of kaolinite. The combined line is actually a composite of three lines

(i) (020) with $d = 4.455$ Å
    $2\theta = 19.91°$ for Cu $K\alpha$ $A = 59$

(ii) (1Ī0) with $d = 4.36$ Å
    $2\theta = 20.32°$ for Cu $K\alpha$ $B = 172$

(iii) (110) with $d = 4.325$ Å
    $2\theta = 20.51°$ for Cu $K\alpha$ integrated intensity 17.

The data for integrated intensity have been taken from Brindley & Robinson (1946). Fig. 3(a) shows that the combined line profile has a range of 1.60° and the angular separation δ between 020 and 1Ī0 is 0.41°. The (110) line, contributes very little to the composite line profile and so has been neglected while separating the profiles of the remaining two lines. Consider the line profiles for the 020 and 1Ī0 reflexions as $f(x)$ and $g(x)$ respectively. For $\delta = 0.41°$, $g(x)$ and $f(x)$ have been obtained from equations (8) and (9). Since applications of equations (4) and (5) show that $\alpha = 0$ and $\beta = 0$, $f(x)$ and $g(x)$ are both symmetrical.

References

AVERBACH, B. L. & WARREN, B. E. (1949). J. Appl. Phys. 20, 885.

BRINDLEY, G. W. & ROBINSON, K. (1946). Miner. Mag. 27, 242.

BRINDLEY, G. W. & NAKAHIRA, M. (1959). J. Amer. Ceram. Soc. 42, 314.

JOHNS, W. D. (1953). Min. Mag. 30, 186.

MITRA, G. B. (1963). Z. Kristallogr. 119, 3/4, 161.

MITRA, G. B. (1964). Acta Cryst. 17, 765.

MITRA, G. B. & MISRA, N. K. (1966). Brit. J. Appl. Phys. 17, 1319.

MITRA, G. B. & BHATTACHERJEE, S. (1969a). Acta Cryst. B25, 1668.

MITRA, G. B. & BHATTACHERJEE, S. (1969b). Amer. Min. 54 (9–10), 1409.

WILSON, A. J. C. (1962). Proc. Phys. Soc. 80, 286.