QUALITATIVE AND QUANTITATIVE STUDY OF STACKING FAULTS IN A HYDRAZINE TREATED KAOLINITE—RELATIONSHIP WITH THE INFRARED SPECTRA

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Abstract—Artificial stacking faults can be created within a well-crystallized kaolinite by intercalating and removing hydrazine. X-ray powder patterns with electron microscopy show that the created defects are $\pm \mathbf{b}/3$ translations with a proportion 0.30. The infrared spectrum of the treated kaolinite is not modified with respect to the starting one. On the other hand, a natural kaolinite containing defects by displacement of Al vacancies in a similar proportion shows an infrared spectrum significantly different from that of a well-crystallized kaolinite. The modification of the infrared spectra of natural disordered kaolinites is then related to the presence of defects by change of Al vacancy positions

INTRODUCTION

It is well known that the infrared spectra of more or less disordered natural kaolinites show appreciable differences in the OH stretching bands. In a well-crystallized kaolinite, four absorption bands are observed at 3695, 3670, 3650 and 3620 cm^{-1}, the 3670 and 3650 cm^{-1} bands being much weaker than those at 3695 and 3620 cm^{-1} (see Figure 1, curve 1). On the contrary, in a highly disordered kaolinite, we observe a decrease of the intensity at 3695 cm^{-1} and the development of one single band between 3640 and 3680 cm^{-1} (see Figure 1, curve 3). Few papers (De Kimpe and Colmet Daage, 1966; Parker, 1969; van der Marel and Krohner, 1969; Noel, 1972; van der Marel and Beutelspacher, 1976) treating the subject attempt to give physical explanation for these observations.

It is also well known that the X-ray powder diffraction diagrams of the more or less disordered kaolinites depends on the degree of disorder in these minerals (Brindley and Robinson, 1946; Murray and Lyons, 1956; Fleurence and Nicolas, 1964). Compared to a well-crystallized kaolinite (Figure 2a), a highly disordered kaolinite (Figure 2c) shows a 'broadening' of the $20(l),13(l)$ X-ray reflections while the $02(l),11(l)$ reflections are smeared out in an almost unmodulated band.

Recent works (Plançon and Tchoubar, 1975, 1976, 1977b) have allowed the determination of the nature of the stacking faults in partially disordered natural kaolinites. Artificial stacking faults can be created within a well-crystallized kaolinite by intercalating

different types of molecules between the layers. In general, the molecules able to enter the interlamellar space are those whose dipole moment and proton affinity are high. The net result of intercalation is to decrease the cohesion forces between layers. The intercalation complexes are nevertheless unstable towards heat, vacuum or water treatment, the molecules leaving the interlamellar space. Removal of intercalated molecules does not restore the initial structure (Wiewiora and Brindley, 1969; Jacobs, 1971). Since the molecules have specific interactions with the surface, it has been thought that these structural differences could find their origin in the way the molecules enter or abandon the interlamellar space. In
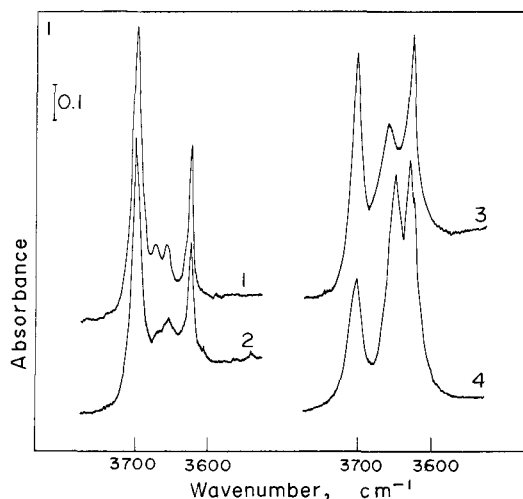

Figure 1. Infrared spectra of a well-crystallized kaolinite (curve 1), of a disordered kaolinite (curve 2), of a highly disordered kaolinite (curve 3) and of a dickite (curve 4), (Noel, 1972).

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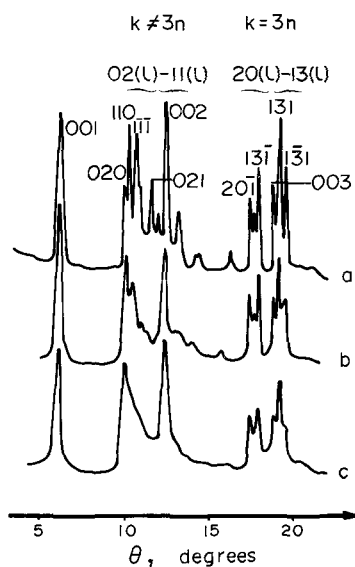
Figure 2. X-ray powder diffraction pattern of (a) well-crystallized kaolinite, (b) disordered kaolinite, (c) highly disordered kaolinite.

this adsorption–desorption process, they could produce changes in the relative positions of the layers in the same crystallite.

The present paper aims to relate experiments which have been performed in order to create artificial stacking faults by intercalating hydrazine within a well-crystallized kaolinite. The structural evolution of the sample is studied by X-ray powder diffraction and is connected to the evolution of the infrared spectra. Finally, conclusions are drawn on the origin of the modification in the infrared spectra of disordered natural kaolinites as compared to well-crystallized samples.

MATERIALS AND METHODS

A less than $2 \mu m$ fraction of a well-crystallized Georgia kaolinite was used for the preparation of a kaolinite–hydrazine complex. Such complexes have been studied previously by Weiss *et al.* (1963) and Ledoux and White (1966). The characteristic d_{001} spacing is observed at 10.40 Å. Although the dipole moment of hydrazine is not very high (2.89), the fact that at least 3 molecules per unit cell can be accommodated in the interlamellar space accounts for its rapid reaction with kaolinite (Cruz *et al.*, 1972). The hydrazine cross-section has approximately the same value as two OH, thus being able to cover the OH surface completely. Hydrogen bonds are formed between the OH and the single pair of electrons of the nitrogen atoms (Ledoux and White, 1966). The complex has been prepared by a modification of the Ledoux *et al.* (1966) procedure. One g of kaolinite was dispersed in 10 ml of hydrazine (Merck, high purity, anhydrous 95%). The suspension was shaken during 3 days and isolated from the air. The sample was

submitted to vacuum (10^{-3} torr) at room temperature in order to eliminate hydrazine. The total collapse of the complex is followed by the disappearance of the *001* reflection at 10.40 Å and the disappearance of the infrared band at 3365 cm^{-1}.

The measurement of the X-ray diffracted intensities was performed by transmission with a diffractometer equiped with a curved quartz monochromator in order to select the Cu Kα_1 radiation. The slits were of a limited height to suppress the umbrella effect and also of a limited width in order to eliminate the convolution of reflection profiles by instrumental functions. The spectra were recorded stepwise at intervals of $0.01°\theta$. At each position, 10^4 photons were counted. The intensities obtained by this procedure were finally corrected for polarization and for absorption; the background scattering was subtracted. All experimental intensities reported in this paper correspond to such corrected values for samples which have been freeze-dried in order to have a powder as little oriented as possible.

The transmission infrared spectra were recorded with a Perkin–Elmer 180 spectrophotometer. One milligram of kaolinite was diluted with approximately 200 mg KBr. The area of the pellet was about 1 cm^2.

EXPERIMENTAL RESULTS

As previously observed (Jacobs and Stercks, 1970; Mata-Arjona *et al.*, 1970), the study of the *001* peak in the X-ray powder diagram of the hydrazine–kaolinite complex shows that kaolinite has been intercalated to a large percentage (*001* peak corresponding to $d_{001} = 10.40$ Å), though a small fraction of unexpanded kaolinite ($d_{001} = 7.15$ Å) remains. It is impossible to determine accurately (for example by using the ratio I_{001} non-expanded kaolinite/I_{001} expanded kaolinite) the amount of non-intercalated kaolinite, because the crystalline structure of the hydrazine–kaolinite complex is unknown.

X-ray results

Figure 3 shows the experimental X-ray powder diagram of the starting Georgia kaolinite, for the regions of *02(l),11(l)* reflections (Figure 3a) and of the *20(l),13(l)* reflections (Figure 3b), respectively. In a previous paper, Plançon and Tchoubar (1977b) have shown that this kaolinite contains a small number of faults, e.g. a proportion $P = 0.03$ of random shifts of layers and $\eta_d = 0.08$ of faults by displacement of the Al vacancies.

Figure 4 shows the X-ray diagram of the same kaolinite after treatment. Comparison of the band profiles of this kaolinite with those of the untreated one shows that:

(1) There is a broadening of the *002* reflection which indicates that the average number of layers within an individual crystallite decreases from 75 to about 40 layers (this determination has been made by means of the Scherrer formula).
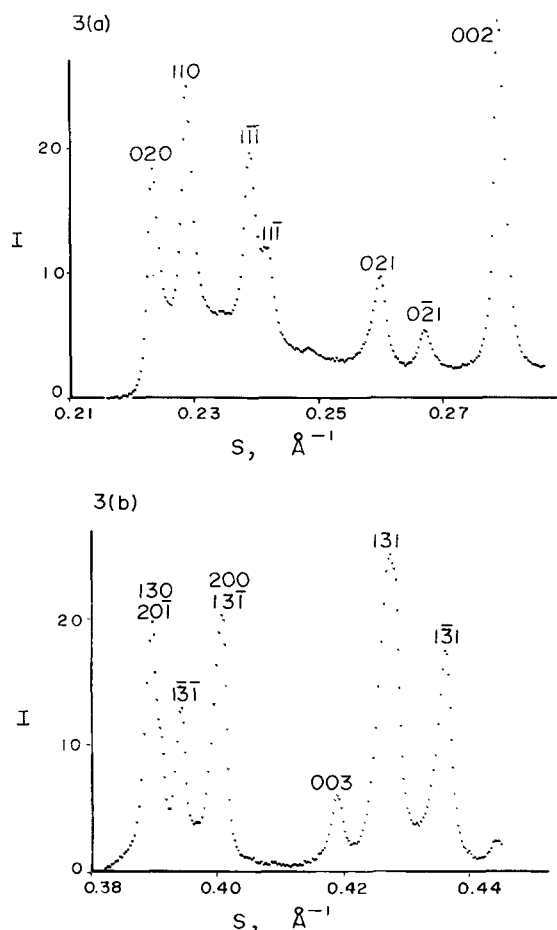
3(a)

3(b)

Figure 3. X-ray powder diffraction pattern of the starting well-crystallized kaolinite. (a) *(02,11)* band profile, (b) *(20,13)* band profile.

Figure 5. Orientation function of the starting kaolinite (curve 1) and of the treated sample (curve 2).

(2) There is a slight evolution of the *20(l),13(l)* band profile. This modification is due not to an increase of random translation between the layers but to an increase of the preferential orientation of the particles parallel to the sample holder in the treated sample (Figure 5, curve 2) relative to that of the starting material (Figure 5, curve 1). Taking into account this
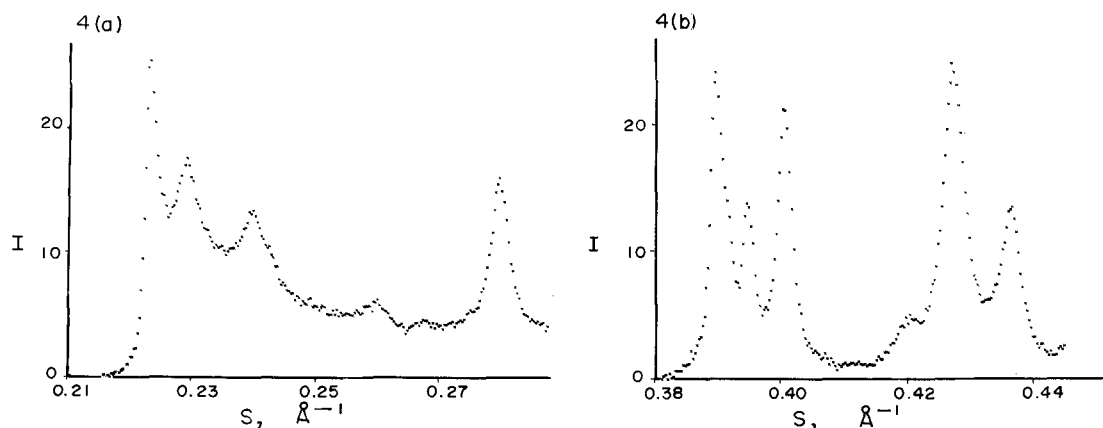
orientation, the best fit between calculated and experimental *(20,13)* band profile is obtained as previously, for a proportion $P = 0.03$ of random defects (Figure 6). (The radius in the layer plane of the coherent volume is equal to 250 Å.)

(3) There is an important modification of the *02(l),11(l)* reflections which is due to the creation of stacking faults without affecting in a sensible manner the *h,3n,l* reflections. The possibility of displacement of octahedral vacancies must be excluded here because it does not lead to a correct agreement between the experimental and theoretical *(02,11)* band profiles. On the other hand, the possibility of $\pm 2\pi/3$ rotations must also be discarded because they should affect greatly the *h,3n,l* reflections (see Plançon and Tchoubar, 1977b) and because the observations of the treated sample by electron microscopy does not show any $\pm 2\pi/3$ rotations among the layers in particles. One can then conclude that by the treatment of the kaolinite by hydrazine and subsequent desorption,

4(a)

4(b)

Figure 4. X-ray powder diffraction pattern of the kaolinite after hydrazine treatment. (a) *(02,11)* band profile, (b) *(20,13)* band profile.

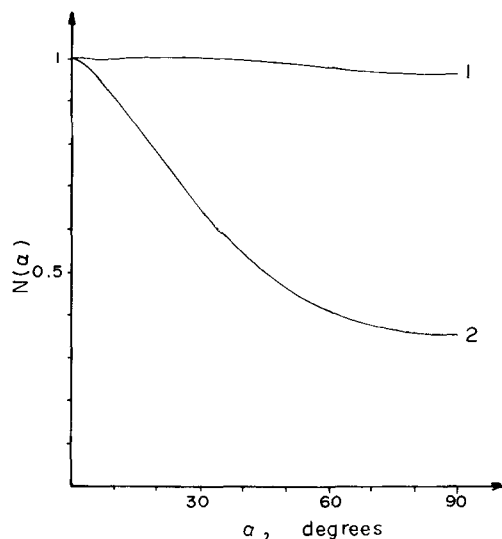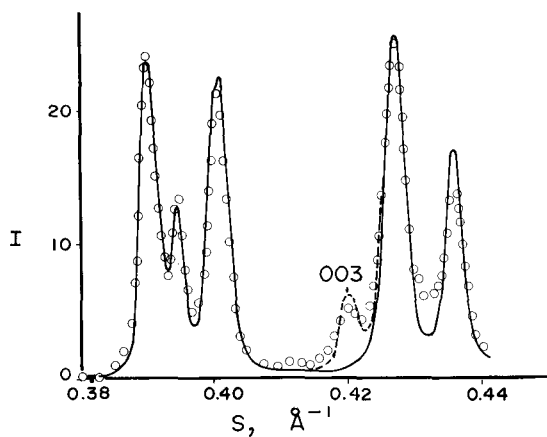Figure 6. Experimental (O) and calculated (——) (*20,13*) band profile of the hydrazine-treated kaolinite.

only **b**/3 translative stacking faults are created. The proportion of $\pm$**b**/3 artificially created defects has been evaluated by using the method proposed by Plançon and Tchoubar (1977a), while taking into account a small proportion of unexpanded kaolinite. Thus, the X-ray diffraction pattern of the treated kaolinite comprises the diffraction by a major proportion of disordered kaolinite mixed with a residual amount of the well-crystallized unexpanded starting material. The optimum agreement (Figure 7) between the experimental and calculated profiles for the *02(l),11(l)* reflections is obtained for 11% (by weight) of unexpanded kaolinite and 89% of disordered mineral. The latter is characterized by a proportion $\eta_t = 0.30$ of $\pm$**b**/3 of translational defects between layers plus $P = 0.03$ and $\eta_d = 0.08$ faults contained in the starting material (for this treated kaolinite, the radius of the coherent volume in the layer plane is equal to 600 Å).

Infrared results

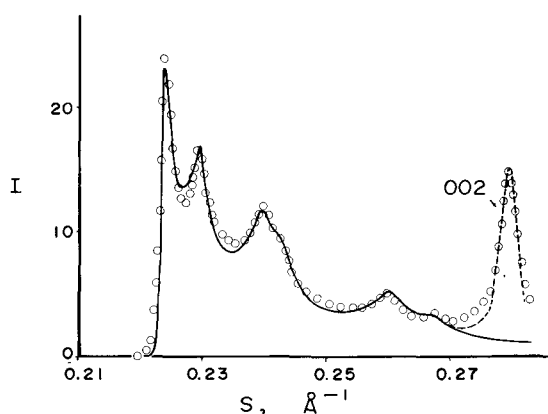The assignment of the OH stretching bands of kaolinite can be summarized as follows: the 3620 cm^{-1} band is attributed to the inner hydroxyls since it is unaffected by deuteration at room temperature (White *et al.*, 1970) or by intercalation of any complexing agent (Ledoux and White, 1966). The multiplicity of the three remaining bands has been the object of numerous hypotheses. All authors agree finally that they must be assigned to the three outer hydroxyls, namely those in the interlamellar space. Farmer (1964) and Farmer and Russell (1964) proposed that the 3695 cm^{-1} band is the in-plane vibration due to the vibrational coupling of the inner three surface hydroxyls in the unit cell. Its transition moment is perpendicular to the layer. The 3670 and 3650 cm^{-1} bands would be two degenerate out-of-plane vibrations of the same hydroxyls, the transition moment lying in the plane of the layer. A study by Samudacheata (1975) concludes that the 3695 and 3670 cm^{-1} bands result from coupled vibrations of two identical hydroxyls. The band at 3650 cm^{-1} would be assigned to another type of OH. This model is in agreement with the OH orientation proposed by Giese and Datta (1973): two OH are tilted by 13° with respect to the *c*-axis, whereas the third one is at 76° from that axis. The infrared spectrum of the starting kaolinite used in this work is shown in Figure 8 (curve 1). The infrared spectrum obtained after desorbing hydrazine is that shown by curve 2 (Figure 8). There is obviously no differences between these two spectra.

The study of the influence of the nature of the stacking faults on the infrared spectra has been completed by comparing the treated sample studied here, with a partially disordered natural kaolinite. This disordered sample exhibits *02(l),11(l)* and *20(l),13(l)* X-ray reflections (Figures 9a and b) close to that of the artificially disordered (treated) sample. The structural study of this natural sample (Plançon and Tchoubar,

Figure 7. Experimental and calculated (*02,11*) band profile of the hydrazine-treated kaolinite.
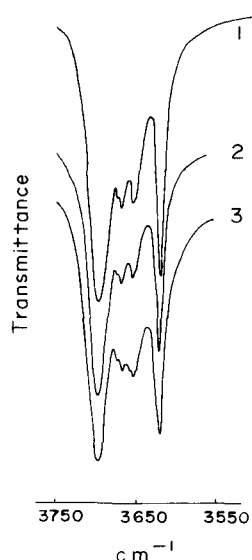

Figure 8. Infrared spectra of the starting kaolinite (curve 1), of the treated kaolinite (curve 2) and of a partially disordered natural kaolinite used for comparison (curve 3).
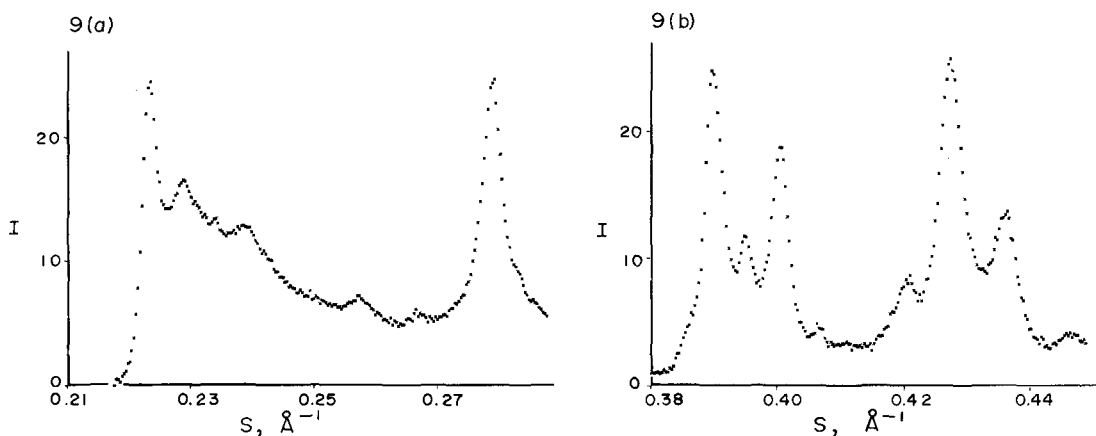
Figure 9. X-ray powder diffraction pattern of the partially disordered natural kaolinite used for comparison (see text). (a) (02,11) band, (b) (20,13) band.

1977b) shows mainly stacking faults by displacement of the Al vacancies (in a proportion $\eta_d = 0.42$), while the other faults are much less important ($P = 0.07$ and $\eta_t = 0.06$). In agreement with Noel's results, the infrared spectrum of this disorganized natural kaolinite is really altered (Figure 8, spectrum 3) compared with that of a well-crystallized sample and that of the hydrazine treated kaolinite (spectra 1 and 2). Compare for instance the intensity of the 3695 cm^{-1} band and the strong band between 3640 and 3680 cm^{-1}.

DISCUSSION

The results obtained by infrared spectroscopy show that an appreciable difference exists between the artificially disordered kaolinite and the natural disordered sample. The only structural differences between these two minerals are in the nature of their defects. Therefore it seems logical to correlate the modification of the OH stretching bands of kaolinites more or less disordered to the presence of faults by displacement of Al vacancies, while the $\pm\mathbf{b}/3$ translative stacking faults created by the hydrazine treatment does not modify appreciably the OH stretching spectra.

The interpretation of the infrared spectra of the kaolin mineral must take into account: (a) the orientation of the OH dipoles related to the electric field in the interlamellar space (Giese and Datta, 1973) and (b) the existence of coupling between the hydroxyl groups (Jacobs, 1971; Cruz et al., 1972; Farmer, 1974; Samudacheata, 1975).

All factors able to alter the symmetry of the crystalline field will modify the intensity and shape of the absorption bands.

The results obtained in this work suggest that faults by displacement of Al vacancies change appreciably the environment of the OH of the inner surface hydroxyls (opposite to the oxygen plane) whereas the translational faults $\pm\mathbf{b}/3$ do not produce such a modification. These conclusions are in agreement with the structural data of Newnham (1961) and

Zvyagin (1960). Translations by $\pm\mathbf{b}/3$ leave the OH groups in a practically identical position relatively to the basal oxygens of the adjacent layer. On the contrary, their mutual positions are different in the case of a B.B superimposition of Al vacancies (kaolinite) and in the case of a B.C superimposition of Al vacancies (dickite). An interpretation of the results obtained by Noel (1972) for highly disordered kaolinites becomes then possible. The conclusion of Noel's work was that the infrared spectrum of a disordered kaolinite can be considered as being intermediate between that of a well-crystallized kaolinite and that of a dickite (Figure 1, curve 4). In dickite, the 3695 cm^{-1} band is strong and the band between 3640 and 3680 cm^{-1} is also intense. It is important to remind that the layer stacking of a dickite presents a regular alternation of the octahedral vacancies between the B and C positions. In a well-crystallized kaolinite, the vacancies always occupy the same position (B or C). In a poorly crystallized kaolinite, a disorder in the octahedral vacancies distribution is observed which includes B.C alternations (Plançon and Tchoubar, 1977b). Therefore, the infrared spectrum of such a poorly crystallized sample should indeed tend towards the OH profile observed in dickite.

The intercalation and further desorption of hydrazine could act in two ways: (a) by allowing the kaolinite layers to slide with respect to each other, and (b) by cleaving the microcrystals in some places.

What happens during cleavage is of course unknown. Since the thickness of the original crystallite is reduced statistically by a factor of two, the treatment has broken the cohesion between the layers. If this cohesion was identical for all the layers within a crystallite, the cleavage energy could reach 20 kcal/g unit cell (Wieckowski and Wiewiora, 1976) and perhaps 30 kcal/g unit cell (Cruz et al., 1972). Obviously the (a) effect demands a lower energy than the (b) effect. However, cleavage planes may contain some characteristics which decrease the cohesion energy (for instance, local concentration of faults or effect of 'bubbles', see Figure 10).
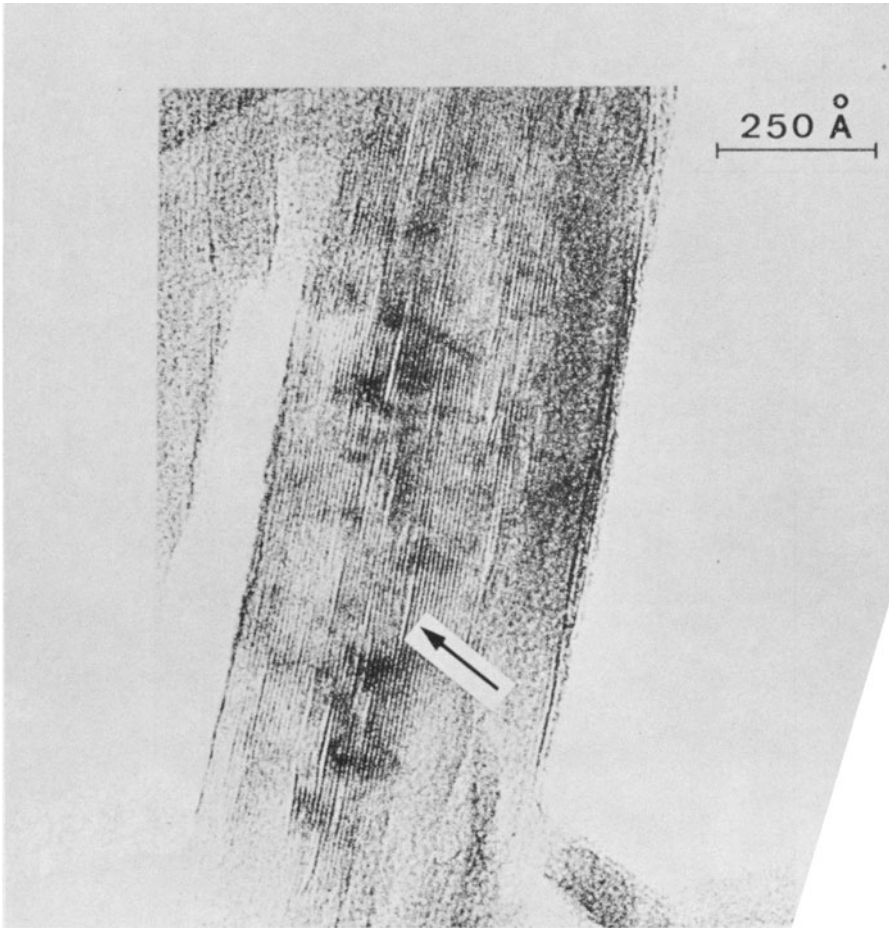
Figure 10. Visualization of the layers of the starting kaolinite by lattice imaging in electron microscopy (photograph by C. Clinard).

REFERENCES

Brindley, G. W. and Robinson, K. (1946) Randomness in the structures of kaolinitic clay minerals: *Trans. Faraday Soc.* **46**, 49–62.

Cruz, M. I., Jacobs, H. and Fripiat, J. J. (1972) The nature of the interlayer bonding in kaolin minerals: *Proc. Int. Clay Conf.*, Madrid, pp. 35–46.

de Kimpe, C. and Colmet Daage, F. (1966) Caractérisation des minéraux kaolinitiques par diverses techniques: *Bull. Gr. Fr. Arg.* **3**, 59–66.

Farmer, V. C. (1964) Infrared absorption of hydroxyls groups in kaolinite: *Science* **145**, 1189–1190.

Farmer, V. C. (1974) *Infrared Spectra of Minerals*, p. 341: Mineralogical Society, London.

Farmer, V. C. and Russell, J. D. (1964) The infrared spectra of layer silicates: *Spectrochim. Acta* **20**, 1149–1173.

Fleurence, A. and Nicolas, J. (1964) Observation sur la notion d'ordre et de désordre de certains minéraux du groupe de la kaolinite: *Bull. Gr. Fr. Arg.* **14**, 149–162.

Giese, R. F. and Datta, P. (1973) Hydroxyl orientation in kaolinite, dickite and nacrite: *Am. Miner.* **58**, 471–479.

Jacobs, H. (1971) Etude des hydroxyles de la kaolinite par spectroscopie infrarouge: Thèse, Université Catholique de Louvain.

Jacobs, H. and Stercks, M. (1970) Contribution à l'étude de l'intercalation du dimethylsulfoxyde dans le réseau de la kaolinite: *Proc. Reunion Hispano-Belge Miner. Arg.*, Madrid.

Ledoux, R. L. and White, J. L. (1966) Infrared studies of hydrogen bonding interaction between kaolinite surfaces and intercalated potassium acetate, hydrazine, formamide and urea: *J. Colloid Interface Sci.* **21**, 127–152.

Mata-Arjona, A., Ruiz-Amil, A. and Inara-Martin, E. (1970) Cinetica del proceso de sorcion del dimetilsulfoxido en caolinita: estudio por difraccion de rayos X: *Proc. Reunion Hispano-Belge Miner. Arg.*, Madrid.

Murray, H. H. and Lyons, S. C. (1956) Correlation of paper-coating quality with degree of crystal perfection of kaolinite: *Clays and Clay Minerals* **4**, 31–40.

Newnham, R. E. (1961) A refinement of the dickite structure and some remarks on polymorphism in kaolin minerals: *Miner. Mag.* **32**, 683–704.

Noel, C. (1972) Interprétation quantitative des bandes de valence OH des phyllosilicates et des amphiboles: Thèse, Université de Louvain.

Parker, T. W. (1969) Classification of kaolinites by infrared spectroscopy, *Clay Miner.* **8**, 1935.

Plançon, A. and Tchoubar, C. (1975) Etude des fautes d'empilement dans les kaolinites partiellement désordonnées—I. Modèle ne comportant que des fautes par translation: *J. Appl. Cryst.* **8**, 582–588.

Plançon, A. and Tchoubar, C. (1976) Etude des fautes d'empilement dans les kaolinites partiellement désordonnées—II. Modèle comportant des fautes par rotation: *J. Appl. Cryst.* **9**, 279–285.

Plançon, A. and Tchoubar, C. (1977a) Determination of structural defects in phyllosilicates by X-ray powder diffraction—I. Principle of calculation of the diffraction phenomenon: *Clays and Clay Minerals* **25**, 430–435.

Plançon, A. and Tchoubar, C. (1977b) Determination of structural defects in phyllosilicates by X-ray powder diffraction—II. Nature and proportion of defects in natural kaolinites: *Clays and Clay Minerals* **25**, 436–450.

Samudacheata, N. (1975) Etude des hydroxyles de la kaolinite par spectroscopie infrarouge: Thèse, Université de Louvain.

van der Marel, H. W. and Beutelspacher, H. (1976) *Atlas of Infrared Spectroscopy of Clay Minerals and their Admixtures*: Elsevier, Amsterdam.

van der Marel, H. W. and Krohner, P. (1969) OH stretching vibrations in kaolinite and related minerals: *Contrib. Min. Petr.* **22**, 73–82.

Weiss, A., Thielepape, W., Göring, G., Ritter, W. and Schäfer, H. (1963) Kaolinit-Einlagerungs-Veirbindungen: *Proc. Int. Clay Conf.*, Stockholm, Vol. 1, pp. 287–305.

White, J. L., Laycock, A. and Cruz, M. I. (1970) Infrared studies of proton delocalization in kaolinite: *Bull. Gr. Fr. Arg.* **22**, 157–165.

Wieckowski, J. and Wiewiora, A. (1976) New approach to the problem of the interlayer bonding in kaolinite: *Clays and Clay Minerals* **24**, 219–223.

Wiewiora, A. and Brindley, G. W. (1969) Potassium acetate intercalation in kaolinite and its removal; effect of material characteristics: *Proc. Int. Clay. Conf.*, Tokyo, Vol. 1, pp. 723–733.

Zvyagin, B. B. (1960) Electron diffraction determination of the structure of kaolinite: *Dokl. Akad. Nauk S.S.S.R.* **130**(5).