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APPEARANCE OF LONG-SPACING REFLECTION LARGER THAN 24 Å FOR GLYCOLATED INTERSTRATIFIED KAOLINITE/SMECTITE

Key Words—Interstratified kaolinite/smectite, Long-spacing.

After publication of the paper entitled "Quantification curves for the X-ray powder diffraction analysis of mixed-layer kaolinite/smectite" (Tomita and Takahashi 1986), the authors were asked several questions concerning the appearance of long-spacing reflection larger than 24 Å for glycolated inter-stratified kaolinite/smectite. Most of the questions doubt the appearance of the long-spacing reflection. This note will attempt to clarify the theoretical basis for the appearance of the peak.

The general intensity equation of Kakinoki and Komura (1952, 1954a, 1954b, 1965) is given by

$$I = NV^2 + \left(\sum_{m=1}^{N-1} (N - m)\mathrm{spur}VFQ^m + \mathrm{conj}\right)$$

In the two layer case, the V, F and Q matrices become

$$V = \begin{pmatrix} F_1F_1^* & F_2F_1^* \\ F_1F_2^* & F_2F_2^* \end{pmatrix}$$

$$F = \begin{pmatrix} p_1 & 0 \\ 0 & p_2 \end{pmatrix}$$

and

$$Q = \begin{pmatrix} p_{11}\exp(-i\phi_1) & p_{12}\exp(-i\phi_1) \\ p_{21}\exp(-i\phi_2) & p_{22}\exp(-i\phi_2) \end{pmatrix}$$

where $\phi_1 = 2\pi d_1(2\sin\theta/\lambda)$ and $\phi_2 = 2\pi d_2(2\sin\theta/\lambda)$. $\mathrm{spur}VFQ^m$ becomes as follows in cases of m = 1 and 2.

$$\mathrm{spur}VFQ = (p_1p_{11}F_1F_1^* + p_1p_{12}F_1F_2^*)\exp(-i\phi_1) + (p_2p_{21}F_2F_1^* + p_2p_{22}F_2F_2^*)\exp(-i\phi_2)$$

$$\begin{aligned}\mathrm{spur}VFQ^2 = {} & (p_1p_{11}p_{11}F_1F_1^* + p_1p_{11}p_{12}F_1F_2^*)\exp(-2i\phi_1) \\ & + (p_1p_{12}p_{21}F_1F_1^* + p_1p_{12}p_{22}F_1F_2^* + p_2p_{21}p_{11}F_2F_1^* + p_2p_{21}p_{12}F_2F_2^*)\exp(-i(\phi_1 + \phi_2)) \\ & + (p_2p_{22}p_{21}F_2F_1^* + p_2p_{22}p_{22}F_2F_2^*)\exp(-2i\phi_2)\end{aligned}$$

Each term in $\mathrm{spur}VFQ^m$ consists of the product of the following three factors,

(1) the product of the probabilities,
(2) the product of structure factors,
(3) the product of phase factors, $\exp(-i\phi_j)$.

Probability p_i should be followed by p_{ij} (j being any value) and the probability p_{ij} should be followed by p_{jk} (k being any value). The factors not satisfying the above condition do not appear in $\mathrm{spur}VFQ^m$.

For a given factor $p_ip_{ij} \ldots p_{lm}$, the corresponding second factor becomes $F_iF_m^*$.

The origin of the coordinates of structure factors in the equation of Kakinoki and Komura (1952, 1954a, 1954b, 1965) is the top (or bottom) of the layer. If the first factor is given by $p_1p_{12}p_{21}p_{12}$, the phase factor becomes $\exp(-2\pi i(d_1 + d_2 + d_1)(2\sin\theta/\lambda))$. The layer sequence is $L_1L_2L_1L_2$. The probability of finding the interlayer spacing $d_1 + d_2 + d_1$ in this case is $p_1p_{12}p_{21}$. In many treatments, the origin of the coordinates of a structure factor is at the middle of the layer, then the interlayer distance between two layers of layer thickness, d_1 and d_2, becomes $(d_1 + d_2)/2$. But, the distance becomes d_1 in the treatment of Kakinoki and Komura (1952, 1954a, 1954b, 1965). Their success in simplifying the intensity equation of Hendricks and Teller (1942) lies in this treatment.

If phases of waves are composed of a phase and the integral multiples of the phase, interference of the waves is intensified when their phases are the integral multiples of 2π. If there are components having a phase and the integral multiples of the phase in the equation of Kakinoki and Komura (1952, 1954a, 1954b, 1965), the intensity corresponding to the points where the phases become the integral multiples of 2π may be not negligible.

Let us divide the equation of Kakinoki and Komura (1952, 1954a, 1954b, 1965) into the sum of the partial sums consisting of a phase and its integral multiples,

$$I = \sum_i A_i$$

$$A_i = \sum_{n=1} (N - m')B(n)\exp(-2\pi\, in\, R_i(2\sin\theta/\lambda))$$

where the value m′ is determined by the relation R_i and n, any two sums A_i and A_j for i = j are not assumed to have common components. If the value B(n) is not negligible for fairly large n, the intensity at $2\sin\theta/\lambda = 1/R_i$ may not be negligible. Since B(n) is the product of the two factors (1) and (2) described previously and

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the magnitude of the factor (2) is comparable those of the other sums A_i, we can judge the degree of the magnitude of B(n) by the value of factor (1).

For a mixed-layer structure of kaolinite/smectite (K = 7.11 Å, S = 17.0 Å, $P_k = 0.835$, $P_s = 0.165$, $P_{sk} = 1$, $P_{ks} = 0.2$, $P_{kk} = 0.8$ and $P_{ss} = 0$, where K is kaolinite layer, S is smectite layer, P_k is the frequency of occurrence of kaolinite layer, P_s that of smectite layer, P_{sk} is the probability that a kaolinite layer succeeds a smectite layer when the first layer is smectite; P_{ks}, P_{kk}, P_{ss} are similarly defined), the transition probabilities are as follows:

in case of m = 0

	Probability	Spacing (Å)	Remarks
S	0.165	17	
K	0.835	7.11	(1)

in case of m = 1

	Probability	Spacing (Å)	Remarks
SK	0.165	24.11	(2)
KS	0.167	24.11	(2)
KK	0.668	14.22	(1)

in case of m = 2

	Probability	Spacing (Å)	Remarks
SKK	0.132	31.22	(3)
SKS	0.033	41.11	
KSK	0.167	31.22	(3)
KKS	0.1336	31.22	(3)
KKK	0.5344	21.33	(1)

Probabilities of 31.22 Å occurring are 0.4326(0.132 + 0.167 + 0.1336)

in case of m = 3

	Probability	Spacing (Å)	Remarks
SKKS	0.0264	48.22	(2)
SKKK	0.1056	38.33	
SKSK	0.033	48.22	(2)
KSKS	0.0334	48.22	(2)
KSKK	0.1336	38.33	
KKSK	0.1336	38.33	
KKKS	0.1069	38.33	
KKKK	0.4275	28.44	(1)

in case of m = 4

	Probability	Spacing (Å)	Remarks
SKKSK	0.0264	55.33	
SKKKS	0.02112	55.33	
SKKKK	0.08448	45.44	
SKSKS	0.0066	65.22	
SKSKK	0.0264	55.33	
KSKSK	0.0334	55.33	
KSKKS	0.02672	55.33	
KSKKK	0.10688	45.44	
KKSKS	0.02672	55.33	
KKSKK	0.1069	45.44	
KKKSK	0.1069	45.44	
KKKKS	0.0855	45.44	
KKKKK	0.342	35.55	(1)

in case of m = 5

	Probability	Spacing (Å)	Remarks
SKKSKS	0.00528	72.33	(2)
SKKSKK	0.02112	62.44	(3)
SKKKSK	0.02112	62.44	(3)
SKKKKS	0.0169	62.44	(3)
SKKKKK	0.0676	52.55	
SKSKSK	0.0066	72.33	(2)
SKSKKS	0.00528	72.33	(2)
SKSKKK	0.02112	62.44	(3)
KSKSKS	0.00668	72.33	(2)
KSKSKK	0.02672	62.44	(3)
KSKKSK	0.02672	62.44	(3)
KSKKKS	0.021376	62.44	(3)
KSKKKK	0.0855	52.55	
KKSKSK	0.02672	62.44	(3)
KKSKKS	0.021376	62.44	(3)
KKSKKK	0.08552	52.55	
KKKSKS	0.02138	62.44	(3)
KKKSKK	0.08552	52.55	
KKKKSK	0.0855	52.55	
KKKKKS	0.0684	52.55	
KKKKKK	0.2736	42.66	(1)

Probabilities of 31.22 Å occurring are 0.224552 (0.02112 + 0.02112 + 0.0169 + 0.02112 + 0.02672 + 0.02672 + 0.021376 + 0.02672 + 0.021376 + 0.02138) where, (1), (2), and (3) contribute to intensities of reflections of 7.11 Å, 24.11 Å, and 31.22 Å respectively.

Existence probabilities of 31.22 Å and 62.44 Å at m = 2 and m = 5 are 0.4326 and 0.224552, respectively. These values are not negligible/small, so the 31.22 Å reflection occurs.

In this calculation, the authors also considered the L-P factors in low angle regions upon the advice of Reynolds (1980, 1983). When random-powder L-P factors were used, a long-spacing around 30 Å did not occur, but such a long-spacing reflection occurred when the L-P factors for oriented crystallites were used. It is important to use good oriented samples to obtain a long-spacing peak for glycolated interstratified mineral of kaolinite/smectite.

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