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# IDENTIFICATION OF ILLITE/SMECTITE BY X-RAY POWDER DIFFRACTION TAKING INTO ACCOUNT THE LOGNORMAL DISTRIBUTION OF CRYSTAL THICKNESS

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**Abstract:** The illite/smectite (I/S) identification diagram of Środoń (1980), which is based on the positions of 003 and 005 reflections, was constructed assuming three even distributions of crystal thickness: 1–8 and 1–14 layers per crystal for random, and 7–14 for ordered interstratifications. At the time, these distributions were regarded reasonable for diagenetic I/S. Recent studies based on TEM and Bertaut-Warren-Averbach analyses demonstrate, however, that authigenic illites and I/S are characterized by a unique type of lognormal distribution of fundamental particles and crystal thicknesses. The present work shows that XRD data support the correctness of the lognormal crystal size distribution model in the case of illites. The 003 vs 005 diagram then was refined using the lognormal model and a new estimate of the mean crystal thicknesses for a given expandability presented by Drits et al.(in press). The new diagram was calibrated using the NEWMOD computer program. Expandabilities obtained from the original diagram are overestimated by up to 5%S with respect to the refined plot. The refined technique yields %S slightly lower than more sensitive high-angle technique, which is based on weak reflections, the positions of which are not crystal-size dependant. NEWMOD simulations of complete XRD patterns in the 2 – 50° 2θ range, based on parameters measured by the refined technique, produced very good fit to real XRD patterns. Minor differences are attributed to an error in estimating the $LpG^2$ factor for smectite used in NEWMOD calculations.

## Introduction

The mixed-layer illite/ smectites (I/S) are the most abundant clay minerals in soils and sedimentary rocks. They are useful in geological studies because the proportion of the component layers is a sensitive indicator of the degree of diagenesis and low-grade metamorphism. Therefore techniques for measuring I : S ratio (expressed as %S) in these minerals are widely used.

X-ray powder diffraction is used for precise identification of mixed-layer I/S. All existing XRD techniques are based on the positions of chosen reflections from XRD patterns of glycolated samples, because the positions are sensitive to the proportion of I/S in mixed-layer minerals. The peak positions also are affected by the type and degree of ordering, the thickness of ethylene glycol–smectite complex (i.e., $d_{001}$ of smectite), and the thickness of mixed-layer crystals (in the low-angle range) (Reynolds 1980).

The latter variable does not affect the positions of high-angle reflections; therefore the I/S identification technique based on two high-angle reflections, 008* and 009 (method I of Środoń 1980) can be regarded as the most precise. However, these reflections are usually relatively weak and may not be measurable for some samples. Therefore, another identification diagram, which uses the positions of two strong reflections migrating from about 15.4 to 17.7° (003) and 26 to 27° 2θ (005) was constructed (method III of Środoń 1980). The positions of these peaks are sensitive to the crystal thickness; therefore all the factors affecting peak positions should be considered when designing the identification diagram.

The diagram based on 003 vs 005 reflections applies to the whole spectrum of I/S composition, random and ordered interstratifications and thickness of ethylene glycol – smectite complex in the range 16.6 – 17.2 Å. The influence of crystal thickness on XRD profile was modeled assuming three even distributions of crystal thicknesses: 1–8 (mean 4.5) and 1–14 (mean 7.5) layers per crystal for random, and 7–14 (mean 10.5) layers per crystal for ordered interstratifications. These values cover the range of crystal thicknesses which, at the time, were regarded reasonable for diagenetic I/S. For random interstratifications, the measurements using two assumed distributions differ by 5% S. For ordered interstratifications, the error due to the selection of one arbitrary distribution could not be evaluated.

Recent studies of Eberl et al. (1990) and Drits et al. (in press and submitted), using transmission electron microscopy (TEM) and Bertaut-Warren-Averbach analysis of XRD data, demonstrate however, that authigenic illites and I/S are characterised by a lognormal distribution of the thickness of fundamental particles and mixed-layer crystals (coherent scattering domains).

* In this paper, illite/smectite reflections are identified by indices of the smectitic component

The lognormal distribution f(T) of crystal thickness (T) can be expressed by the following equation (Drits et al., in press):

$$f(T) = \frac{1}{\beta T \sqrt{2\pi}} \exp - \left[ \frac{(\ln T - \alpha)^2}{2\beta^2} \right]$$

where $\alpha$ *and* $\beta^2$ are distribution parameters which correspond to the mean value and the variance of lnT, respectively.

A unique type of lognormal thickness distribution was established, using TEM data, for fundamental particles of illites and I/S and it is described by the following experimental relationships between $\alpha$, $\beta^2$ and $T_n$ (mean crystallite thickness) :

$$\alpha = 0.9485 \ln T_n - 0.017$$
$$\beta^2 = 0.103 \ln T_n + 0.034$$

Using these relationships, Drits et al. (in press) modified the Scherrer technique for crystal thickness measurement, and measured mean crystal thickness for a range of I/S minerals. These measurements were applied in the present study to refine method III of Środoń (1980).

The purpose of this study is:

(1) to investigate the effect of mean crystal thickness and crystal thickness distribution on the characteristics of XRD reflections;

(2) to refine the original diagram (method III) of Środoń (1980) by taking into account the lognormal distribution of crystal thickness and the new measurements of the mean crystallite thickness for a given expandability made by Drits et al. (in press);

(3) to verify the modified method by comparing it with another diagram based on two high-angle reflections. In addition, an attempt was undertaken to find the best fit between experimental and computer-simulated patterns for XRD profiles in the 2 – 50° 2θ range.

## Methods

Theoretical XRD (00*l*) patterns were calculated using NEWMOD computer program (Reynolds 1985) modified by R.C. Reynolds to accept distributions of crystal thicknesses from an external file (this version of the program is called NEWMODSKY). For practical reasons, it is assumed that a maximum crystallite thickness ($T_{max}$, crystal thickness expressed as number of layers) used for a given distribution equals 5 x $T_n$. The frequency of lognormal distribution for this $T_{max}$ falls below 0.001 of the maximum frequency.

The experimental XRD patterns used in this study were the following: a set of dehydrated samples of illite/smectites (potassium saturated and dehydrated by heating) recorded on a Siemens D-500 diffractometer (in Boulder, Colorado) characterized by Drits et al. (in press), and samples of Na-saturated and glycolated illite/smectites recorded on a Philips diffractometer (in Kraków, Poland).

In all calculations the following NEWMOD default parameters were applied:

lambda 1.5418 Å, divergence slit 1°, goniometer radius 20 cm, sample length 3.6 cm, soller slit 1 – 6.6°, soller slit 2 – 2°, quartz ref.int. 10000, sigmastar 12° (standard deviation of the orientation function), mustar 45.

The goniometer radius and sample length used in calculations were not always equal those of the experimental configurations. These parameters however, account for intensity loss only at very low diffraction angles (from 0 to 5° 2θ) (Reynolds 1985-1994).

Varying the orientation coefficient (sigmastar), the parameter which influences the Lorentz-polarization factor, did not affect the peak shapes to a measurable extent. As was shown by Reynolds (1986), sigmastar values may range from 4° to 30° for XRD preparations that are oriented using different techniques. We compared the shapes of 001 reflection for computer simulations adopting these two extreme values and the standard one (i.e., 12°): the peaks almost perfectly coincided.

## Results

### (I) The effect of mean crystal thickness and crystal thickness distributions on the characteristics of XRD peaks.

The factors that affect peak position, peak width at half height and peak shape were investigated. The experimental XRD patterns of dehydrated mixed-layer I/S samples were used in order to eliminate the effects of mixed-layering. Samples containing < 20 nm thick crystallites were chosen for study to minimize the effects of instrumental broadening and $K\alpha_1 - K\alpha_2$ separation (Drits et al., in press).

The theoretical XRD patterns both with even and lognormal crystal thickness distributions were produced in NEWMOD using the values of mean crystal thickness $T_n$ calculated from 001 reflection by Drits et al. (in press), the $d_{001}$ calculated from 005 reflection (for which there is no crystal thickness effect on peak position) and the chemical composition of the relevant clays. The comparison between theoretical and experimental profiles is presented in Table1. The following observations were made:

(1) For the calculated patterns, both lognormal and even models reproduce peak positions very accurately. The differences between experimental and theoretical peak positions as well as between the two theoretical models, are not systematic and generally within the measurement error (+/- 0.02° 2θ). However for fined-grained sample 2M9, differences up to 0.08° 2θ were observed. The effect of crystal thickness on peak position is controlled by the mean thickness.

(2) The effect of distribution on peak broadening is very minor but systematic. For most peaks, even distribution

**Table 1:** A comparison among the position (2θ) and broadening (β cosθ) of 001, 002, 003 and 005 reflections from experimental patterns of dehydrated illite/smectites, with those from theoretical profiles adopting even and lognormal crystallite thickness distributions. For each sample, an original smectite content (%S) and a mean number of layers in crystallites ($T_n$, calculated from 001 reflection by Drits et al., in press) are presented.

| SAMPLES | 001 | 002 | 003 | 005 |
|---|---|---|---|---|
| **LF10** | 6%S, $T_n$ = 14.1 | | | |
| 2θ | 8.83 | 17.77 | 26.8 | 45.42 |
| β cosθ | 0.35 | 0.37 | 0.39 | 0.49 |
| NEWMOD- logn. distribution | | | | |
| 2θ | 8.82 | 17.76 | 26.8 | 45.44 |
| β cosθ | 0.35 | 0.33 | 0.34 | 0.34 |
| NEWMOD- even distribution | | | | |
| 2θ | 8.8 | 17.76 | 26.8 | 45.44 |
| β cosθ | 0.36 | 0.37 | 0.38 | 0.38 |
| **Zempleni** | 15%S, $T_n$ = 9.8 | | | |
| 2θ | 8.79 | 17.71 | 26.71 | 45.27 |
| β cosθ | 0.54 | 0.54 | 0.59 | 0.76 |
| NEWMOD- logn. distribution | | | | |
| 2θ | 8.77 | 17.7 | 26.72 | 45.29 |
| β cosθ | 0.52 | 0.50 | 0.50 | 0.50 |
| NEWMOD- even distribution | | | | |
| 2θ | 8.72 | 17.68 | 26.72 | 45.28 |
| β cosθ | 0.49 | 0.51 | 0.52 | 0.54 |
| CH5 | 37%S, $T_n$ = 6.9 | | | |
| 2θ | 8.74 | 17.73 | 26.81 | 45.42 |
| β cosθ | 0.75 | 0.81 | 0.91 | 1.15 |
| NEWMOD- logn. distribution | | | | |
| 2θ | 8.7 | 17.7 | 26.8 | 45.42 |
| β cosθ | 0.76 | 0.71 | 0.73 | 0.74 |
| NEWMOD- even distribution | | | | |
| 2θ | 8.66 | 17.68 | 26.8 | 45.42 |
| β cosθ | 0.67 | 0.72 | 0.75 | 0.77 |
| 2M9 | 88%S, $T_n$ = 6.8 | | | |
| 2θ | 8.78 | 17.76 | 26.81 | 45.54 |
| β cosθ | 0.74 | 0.88 | 1.09 | 1.53 |
| NEWMOD- logn. distribution | | | | |
| 2θ | 8.7 | 17.74 | 26.86 | 45.52 |
| β cosθ | 0.76 | 0.72 | 0.72 | 0.73 |
| NEWMOD- even distribution | | | | |
| 2θ | 8.68 | 17.72 | 26.86 | 45.52 |
| β cosθ | 0.67 | 0.72 | 0.75 | 0.77 |

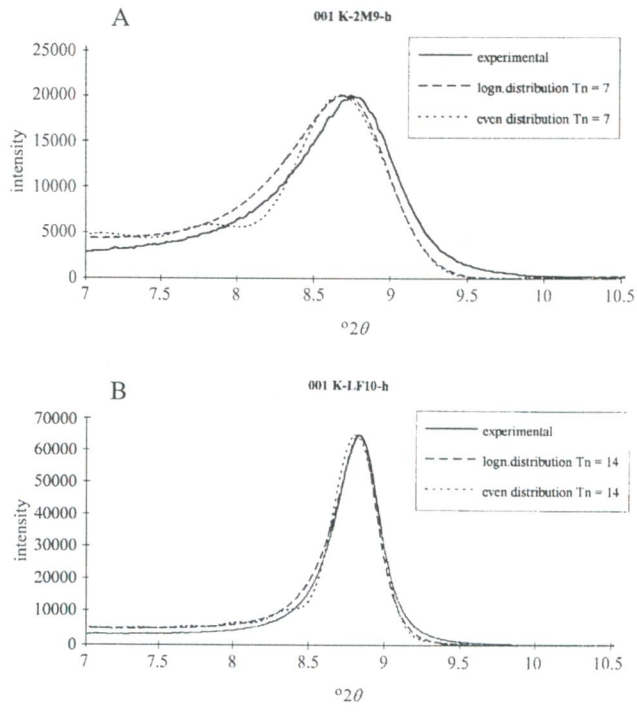


**Fig. 1.** NEWMOD modelling of 001 reflections from XRD patterns of dehydrated illite/smectites for samples 2M9 (A) and LF10 (B) using lognormal and even crystallite thickness distributions, and the values of mean crystal thickness calculated from 001 reflection by Drits et al. (in press). Potassium content applied in the calculations as for pure illite (0.9/ $O_{10}(OH)_2$).

gives values of β cosθ bigger by up to 0.04° 2θ than lognormal distribution. However, this is not the case for the 001 reflection of three fine-grained samples (Zempleni, CH5, 2M9): the values of β cosθ are smaller for even distribution comparing with lognormal by up to 0.09° 2θ. This exceptional behaviour of the 001 peak is due to the fact that broadening of the 001 reflection is systematically higher than other reflections for lognormal model, and lower for even model and these differences increase for fine-grained samples.

(3) For natural samples, peak broadening increases systematically with angle, which has been interpreted as strain-type broadening by Drits et al. (in press). Therefore, only the shapes of 001 reflections can be modeled precisely using NEWMOD, which cannot handle strain-type broadening. In order to perform fitting, background was first removed from the experimental reflections. Flat background was assumed and the minimum intensity value recorded in the analyzed angular range was set to zero. Then intensities were normalized to the maximum intensity.

Fig. 1 A and B show that lognormal model reproduces the experimental shapes much better than the even model, but still the lognormal fit is not perfect: the modeled intensities are too low at the high-angle tail and too high at the low angle tail. The position of maximum intensity is slightly displaced towards low angles. The theoretical reflections illustrated in Fig. 1 were calculated assuming a K content for pure illites i.e., 0.89 atoms of K in structural formula. However, as the samples are heated and K-saturated illite/smectites, we can expect that their K content is lower than that found in pure illites (LF10 originally contained 6 %S, 2M9 - 88 %S). If we then use in NEWMOD calculations a lower K content (LF10: 0.5, 2M9: 0.3 atoms of K/$O_{10}(OH)_2$), we obtain almost a perfect fit for the lognormal model (Fig. 2A and B). The desired adjustment of modeled peak shape results from the modification of the $LpG^2$ function (see Moore & Reynolds, 1989, p.88): a lower K content steepens the slope of the $LpG^2$ in 7.5 – 10° 2θ range. A similar effect on the peak shape can be achieved

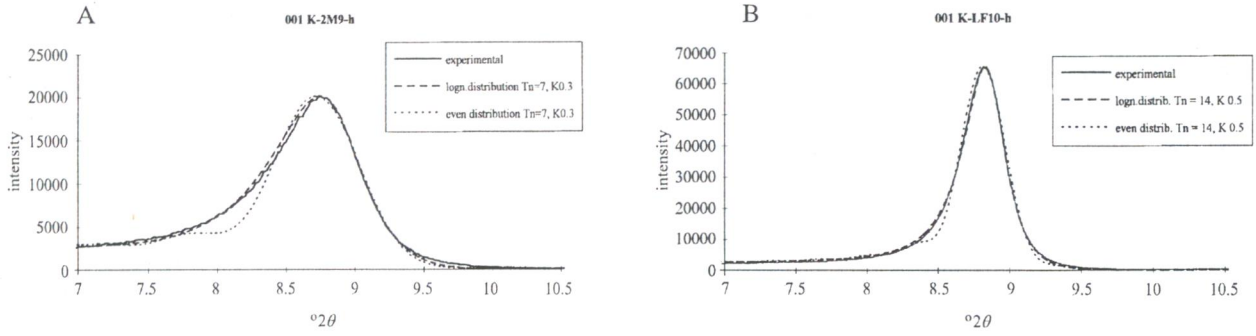


**Fig. 2.** NEWMOD modelling of 001 reflections from XRD patterns of dehydrated illite/smectites for samples 2M9 (A) and LF10 (B) using lognormal and even crystallite thickness distributions. Better fit than in Fig. 1 obtained by lowering potassium content to 0.3/ $O_{10}(OH)_2$ for 2M9 and 0.5/$O_{10}(OH)_2$ for LF10.

by increasing the Fe content (from 0.1 to 1 atoms of Fe in structural formula for the 2M9 sample) which causes a slight shift of the $LpG^2$ function towards high-angles. This modification, however, is not justified considering the chemical composition of the investigated clays.

Approximate analyses of higher order reflections were made by imitating strain-type broadening using crystal size broadening, that is, by fitting higher order reflections with progressively finer lognormal crystal thickness distributions. For the 005 reflection, which is situated in the angular range having flat $LpG^2$ function, a perfect fit between the experimental data and the lognormal model was obtained (Fig. 3A and B). For the even model, misfit similar to 001 reflection is observed.

The presented results indicate that a lognormal distribution of crystal thickness allows for very precise modelling of both peak positions and shapes of XRD reflections of illite. Peak positions in the low-angle range are affected by the mean crystal thickness; so selection of mean thickness is crucial for %S measurements if %S is based on the positions of low-angle reflections.

## (II) Refinement of the I/S identification diagram (method III of Środoń 1980)

The original identification diagram (method III) of Środoń (1980), based on two reflections in the range 15.4 to 17.7° 2θ (003) and 26 to 27° 2θ (005), was refined by taking into account:

— the lognormal distribution of crystal thicknesses, and

— the new estimates of mean crystallite thickness ($T_n$) for a given expandability (%S) from the experimental data of Drits et al. (in press).

The comparison between the values of mean crystallite thickness for a given expandability adopted in the original plot of Środoń (1980) and in the modified one is illustrated in Fig. 4.

A new diagram (Fig. 5) was constructed from the data generated by NEWMOD. The calculations were performed on the whole range of I/S composition (every 10%S, and every 5%S close to the illite end), assuming random interstratification (R0) in the interval 100 to 30%S, partly ordered (R0.5): 60 to 30%S, and ordered (R1): 50 to 20%S, (R2): 20 to 15%S and (R3): 20 to 2%S. The diagram was calibrated for the following values of the thickness of

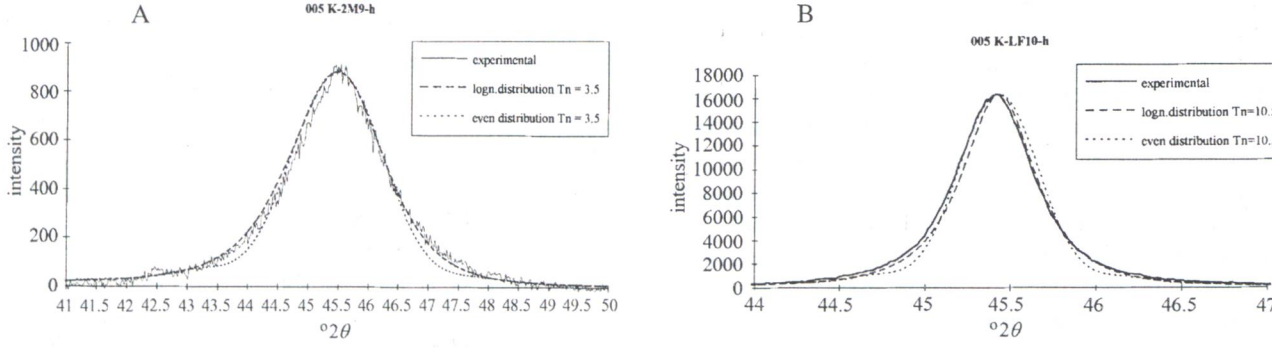


**Fig. 3.** NEWMOD modelling of 005 reflections from XRD patterns of dehydrated illite/smectites for samples 2M9 (A) and LF10 (B) using lognormal and even crystallite thickness distributions. Strain-type broadening of experimental reflections was approximated by lowering the $T_n$ values used in the calculations: $T_n$ = 3.5 for 2M9 and $T_n$ = 10.5 for LF10. Compare with Fig. 2, and see text for details.

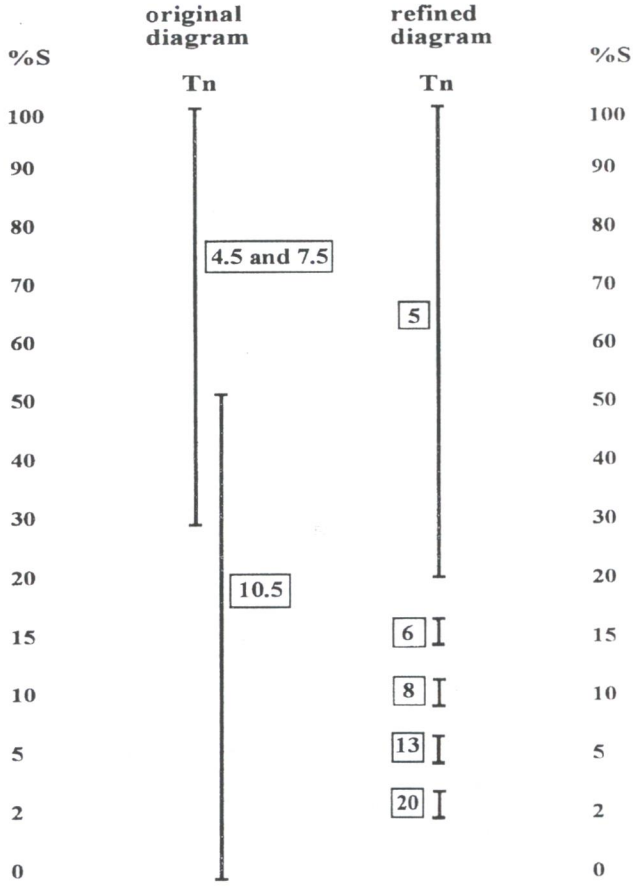


**Fig. 4.** The comparison of the mean values of crystallite thickness, $T_n$ (the numbers in frames), used for different expandabilities (%S) in the original I/S identification plot of Środoń (1980), based on 003 and 005 reflections, and in the refined version of this diagram.

ethylene glycol–smectite complex: 16.6, 16.7, 16.9 and 17.2 Å.

The following observations were made:

1. Crystal thickness affects measurably only the position of the 003 reflection.
2. For random interstratifications, the refined diagram and the original version of the diagram computed for 1–8 layers per crystal give comparable results (the differences are within the measurement error: +/- 0.02° 2θ).
3. For random interstratifications, the results obtained from the version of the original diagram assuming 1–14 layers per crystal are overestimated by up to 5 %S compared with the modified plot. The error increases with decreasing expandability.
4. For ordered interstratifications composed of:
   - ✦ 50 - 20%S, the original plot overestimates results by 3-5%S;
   - ✦ 15 - 10%S, the results obtained from the two diagrams are the same, because $T_n$ values used in the both diagrams are very similar;
   - ✦ 5 - 2%S, the original plot underestimates readings by 2-3%S.

These disparities seem to be mainly due to the differences in the values of mean crystal thickness for a given expandability, because the shape of the crystal thickness distributions does not affect the peak positions measurably.

## (III) The verification of the modified diagram

The modified method has been tested in two ways:

(1) by comparing %S and the thickness of ethylene glycol–smectite complex obtained for a range of natural samples using Fig. 5 and the identification technique based on two reflections in the range 42 – 48° 2θ (008 and 009), which are not dependant on crystal thickness (Fig. 4 in Środoń 1980);

(2) by finding the best fit between experimental and NEWMOD patterns for the 2 – 50° 2θ range, taking into account both the positions and the shapes of reflections.

The positions of high-angle peaks do not react to crystal thickness because the $LpG^2$ function is very flat in this range. Additionally, the migration of these peaks produced by a given difference in %S or smectite $d_{001}$ is three times more pronounced than in case of 003 and 005 peaks, leading to a much higher sensitivity for the former technique. However, high-angle peaks are relatively weak, and may not be measurable for some samples. In addition, the reflections merge at high illite content. Thus this method can be regarded as the most precise (i.e., the standard one) if the above mentioned limitations are avoided. The experimental profiles of I/S used in this study include 42 – 48° 2θ reflections conspicuous enough to be measured properly.

The differences between the results obtained from the two techniques (Fig. 6) are within 7 %S and 0.1 Å for $d_{001}$ of smectite. These differences do not depend on %S or ordering. The differences in $d_{001}$ of smectite are not systematic. The 003 vs 005 technique in most cases underestimates %S.

In order to understand these results, an attempt was made to find the best fit between the experimental and NEWMOD diffractograms in the entire 2 – 50° 2θ range, taking into account both the positions and the broadening of all reflections. To avoid additional complications due to ordering, natural samples of random interstratified I/S were chosen (2M9, 2M3, R-49, 561, G11/1). The computer simulations of diffractograms were produced using values of %S and $d_{001}$ of smectite obtained from the two identification diagrams described in the previous section i.e., 003 vs 005 and 008 vs 009 techniques. All calculations were performed adopting lognormal distributions of crystal thicknesses and two values of the mean crystal thickness: $T_n = 5$ as used for randomly interstratified clays in the modified technique, and $T_n = 6$ for comparison. It was found that the calculations using $T_n = 5$ produced peak broadening closer to the

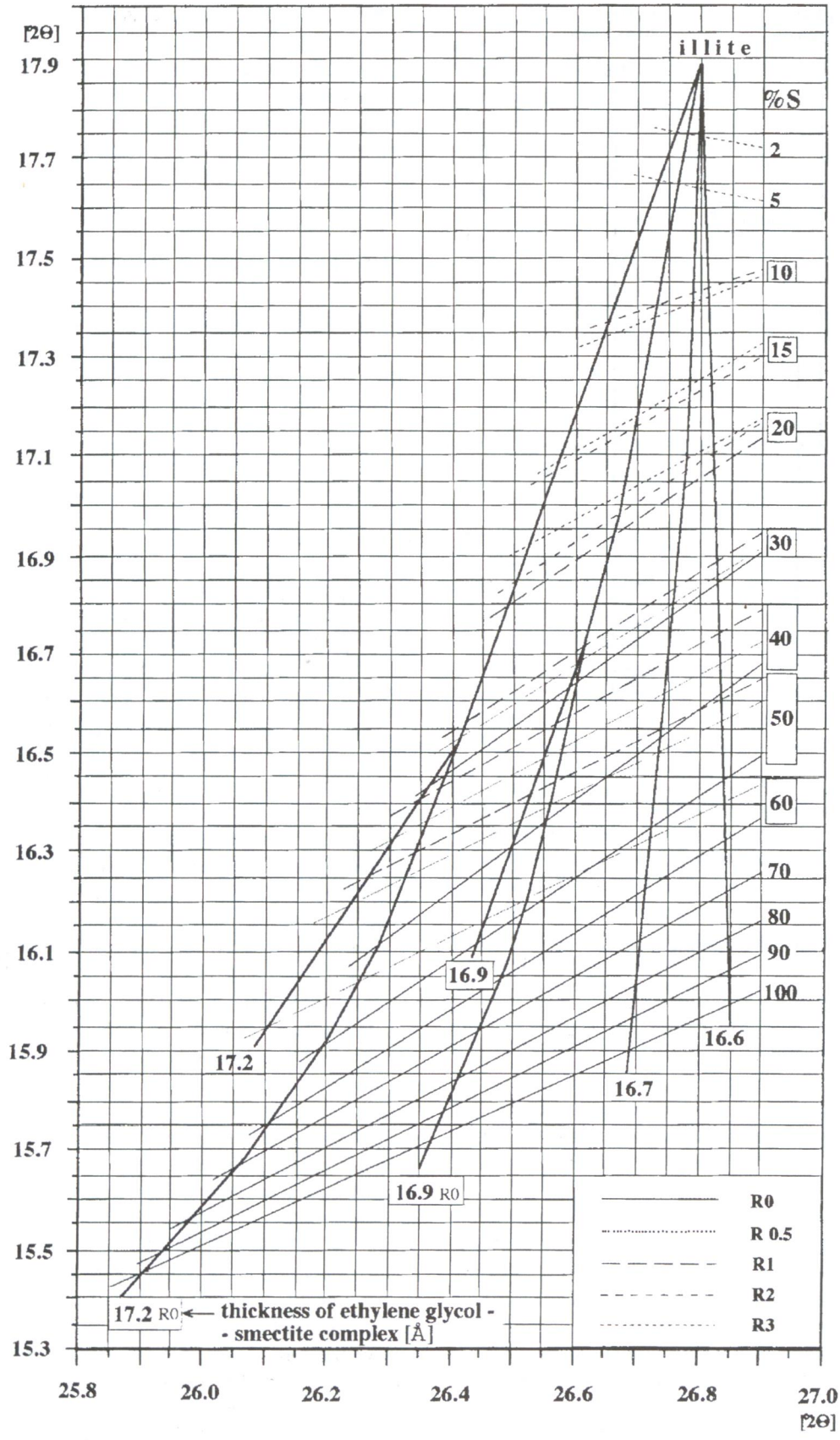


**Fig. 5.** The refined version of I/S identification diagram of Środoń (1980) based on two reflections in the range 15.4 to 17.7° (003) and 26 to 27° 2θ (005). R0 — random interstratification; R0.5, R1, R2, R3 — ordered interstratifications.

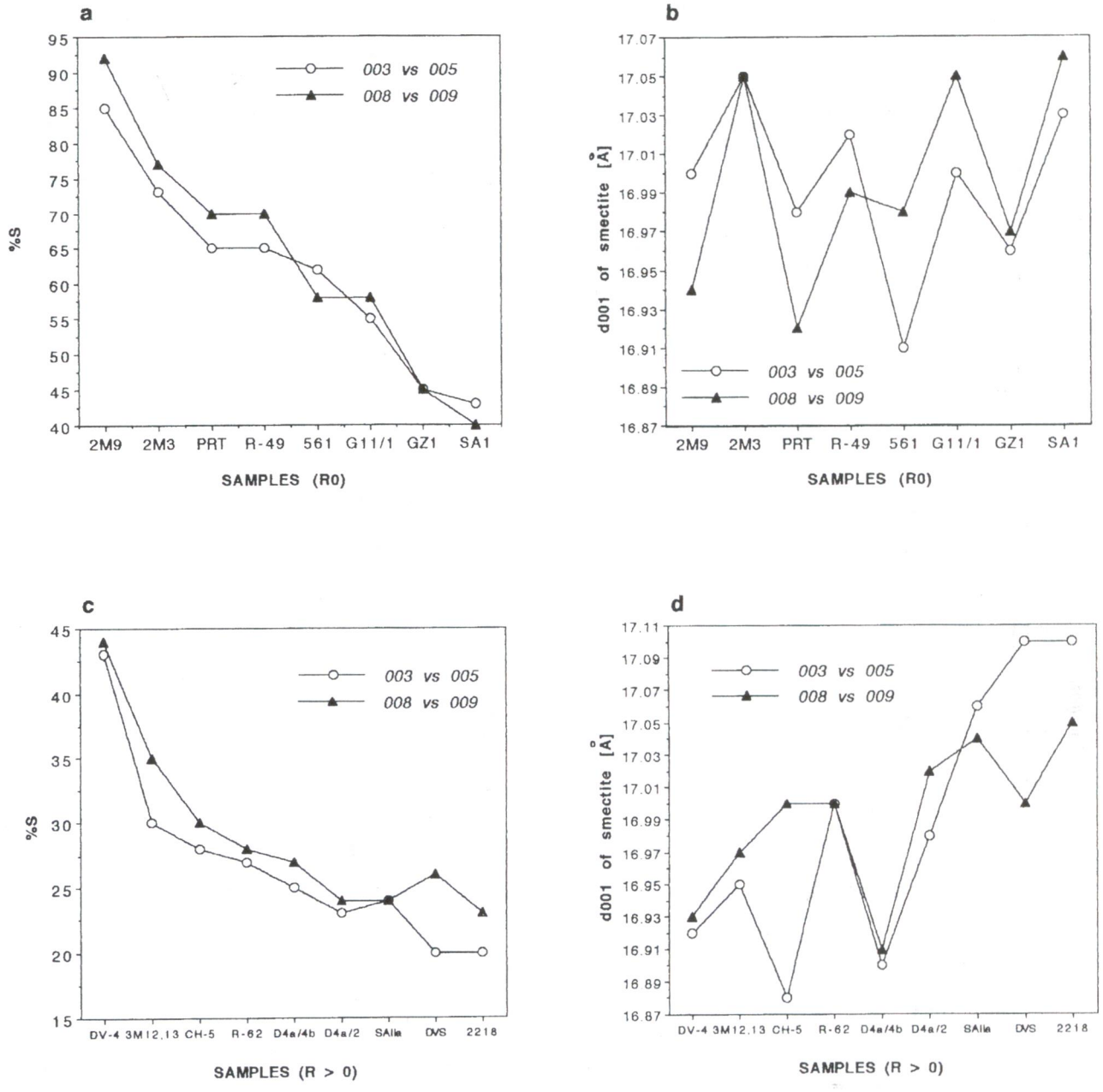


**Fig. 6.** The comparison of the values of %S and $d_{001}$ of smectite estimated for the samples of random (a and b) and ordered (c and d) interstratified illite/smectites from the two identification techniques: 003 vs 005 (circles) and 008 vs 009 (triangles). Samples are arranged according to the increasing smectite content.

experimental data than simulations with $T_n = 6$ (except for the 002 reflection). Therefore, we limited our consideration to the simulations using $T_n = 5$.

Fig. 7 illustrates the results of this excercise for 001, 002, 003, 005 and 008 reflections. The very weak 004, 006 and 009 peaks were neglected.

Peak positions and shapes also were analysed after fitting the experimental patterns with the calculated ones using the procedure described earlier for fitting the diffractograms of dehydrated samples. Fig. 8 illustrates an example of such fitting for the glycolated sample 2M3. Almost identical relationships between experimental and calculated XRD profiles also were obtained for two other samples (2M9 and G11/1).

The following observations were made after analysing Fig. 7 and 8:

1. For 001, 003, 005, and 008 reflections the fit of peak position, broadening and intensity is relatively good whichever technique is used. Among the studied samples, the three most smectitic ones (>60%S) yield the best fit of peak positions. The other two samples show a worse fit. Probably the random model does not describe these samples prop-

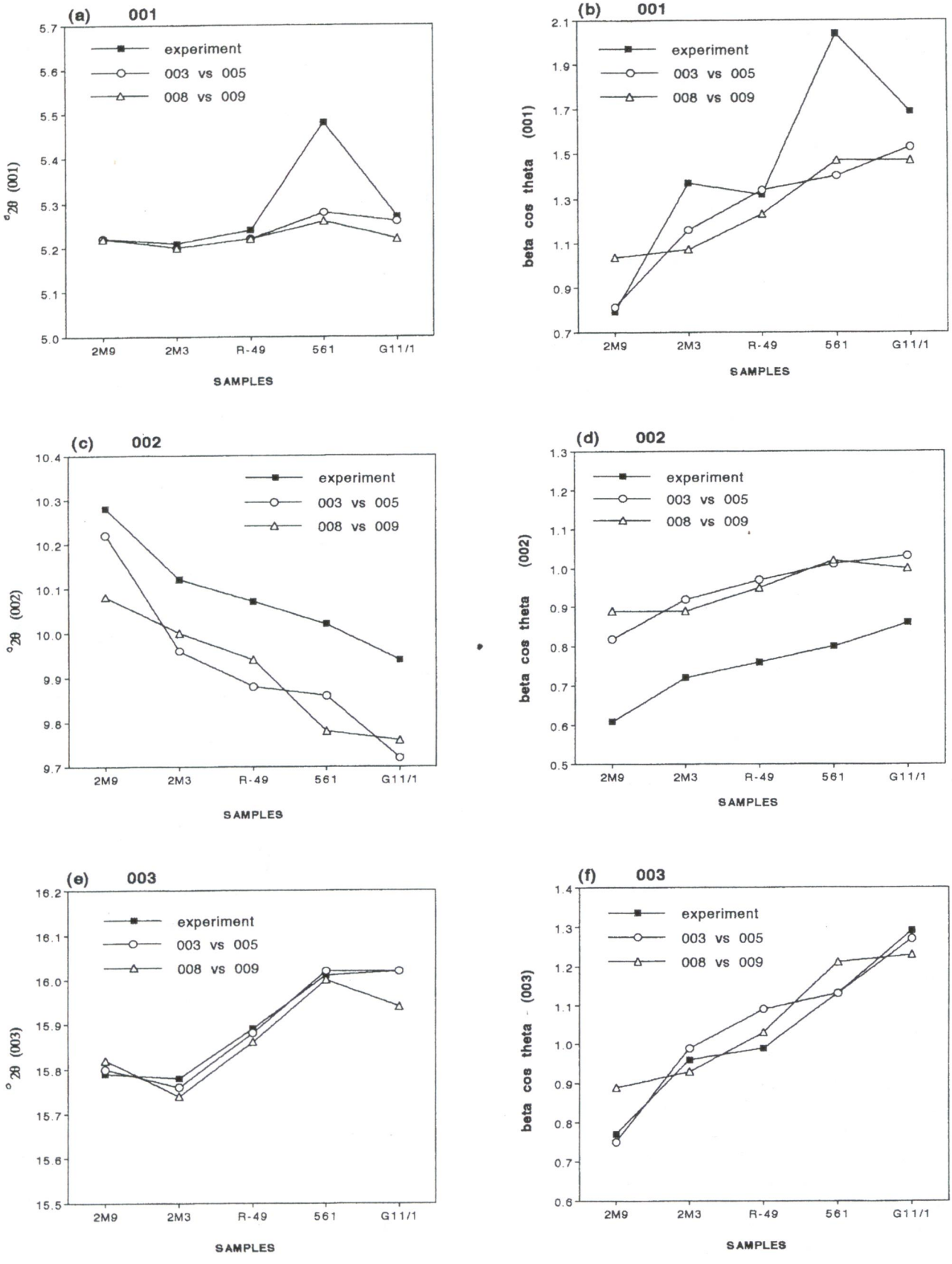


**Fig. 7.** The comparison of the position (2θ) and broadening ($\beta \cos\theta$) of 001 (a, b), 002 (c, d), 003 (e, f), 005 (g, h) and 008 (i, j) reflections from experimental patterns of randomly interstratified illite/smectites (squares) and NEWMOD calculations using %S and $d_{001}$ of smectite obtained from the two identification diagrams: 003 vs 005 (circles) and 008 vs 009 (triangles). The NEWMOD calculations were performed for $T_n = 5$.

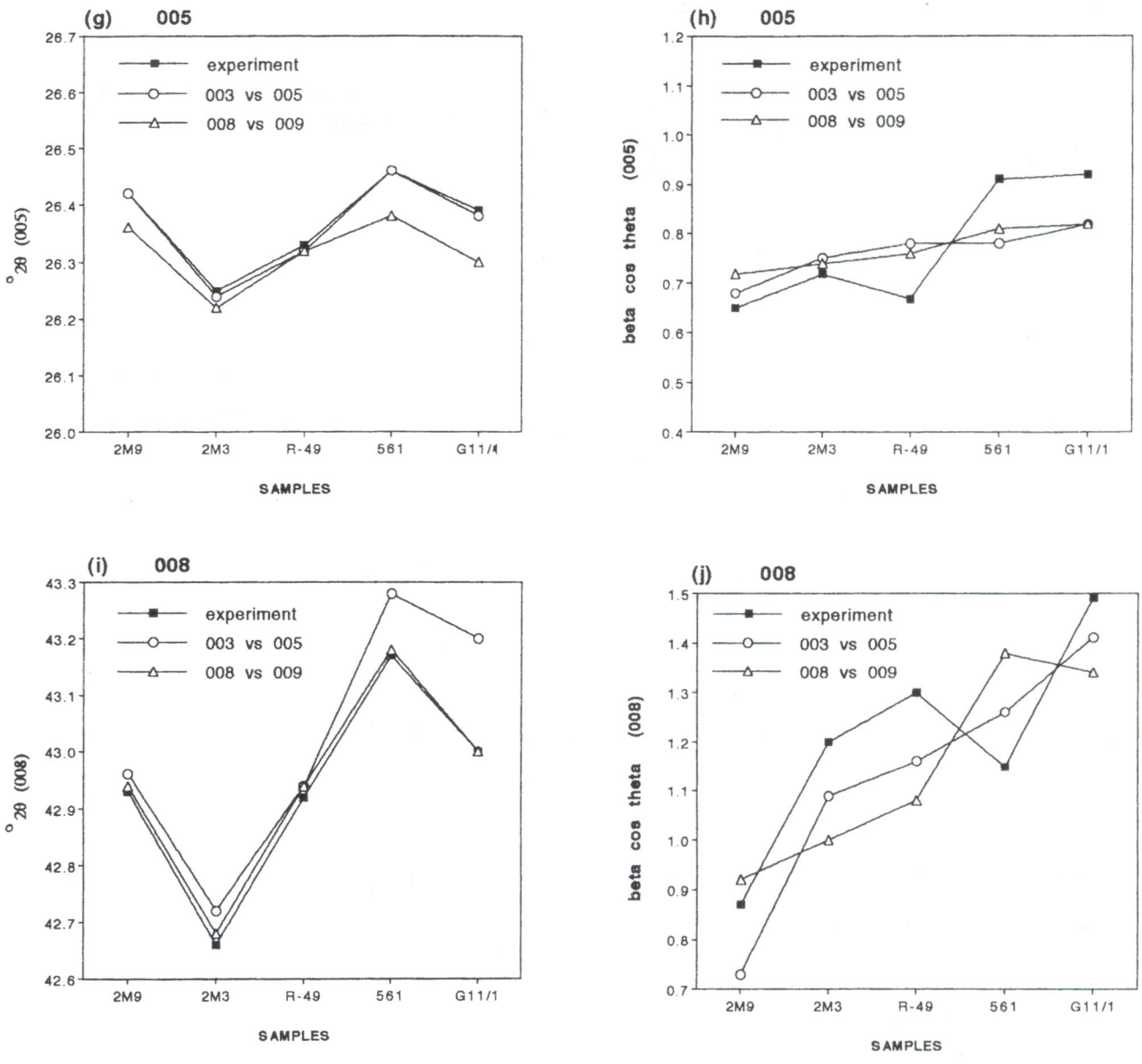


**Fig. 7 (continued):** The comparison of the position (2θ) and broadening ($\beta \cos\theta$) of 001 (a, b), 002 (c, d), 003 (e, f), 005 (g, h) and 008 (i, j) reflections from experimental patterns of randomly interstratified illites/smectites (squares) and NEWMOD calculations using %S and $d_{001}$ of smectite obtained from the two identification diagrams: 003 vs 005 (circles) and 008 vs 009 (triangles). The NEWMOD calculations were performed for $T_n = 5$.

erly (in particular sample 561 may be partially ordered, which would explain anomalous displacement and broadening of the 001 reflection).

2. Reflection 002 behaves anomalously: misfit similar to that described for 001 illite reflection (Fig. 1) is observed, that is, the modeled intensities are too low at the high-angle tail and too high at the low angle tail and the position of maximum intensity is displaced towards low angles (displacement ranges from 0.05 to 0.25° 2θ), and, additionally, the calculated reflections are broader by 0.2 – 0.3° 2θ than the experimental ones (Fig. 7).

3. The background between peak pairs 003 – 004 and 005 – 006 is much less raised in the calculated than in the experimental patterns.

4. 004 reflection is much weaker.

We were not able to improve the fit using the two-component model (changing %S, ordering or Fe content). Similar misfit also was produced when the 3-component model (3COMP program of R.C. Reynolds) with 2 – 5% vermiculite or chlorite as a third component (both di or trioctahedral), was used (Fig. 9a). However, such 3-component model seem to explain the differences between estimates of %S using the two techniques (i.e., 003 vs 005 technique underestimates and 008 vs 009 technique overestimates %S), thus indicating that in natural I/S samples small amounts of 14 Å component might be present (Fig. 9a). To examine this possibility we compared the relationships between %S obtained from the two techniques

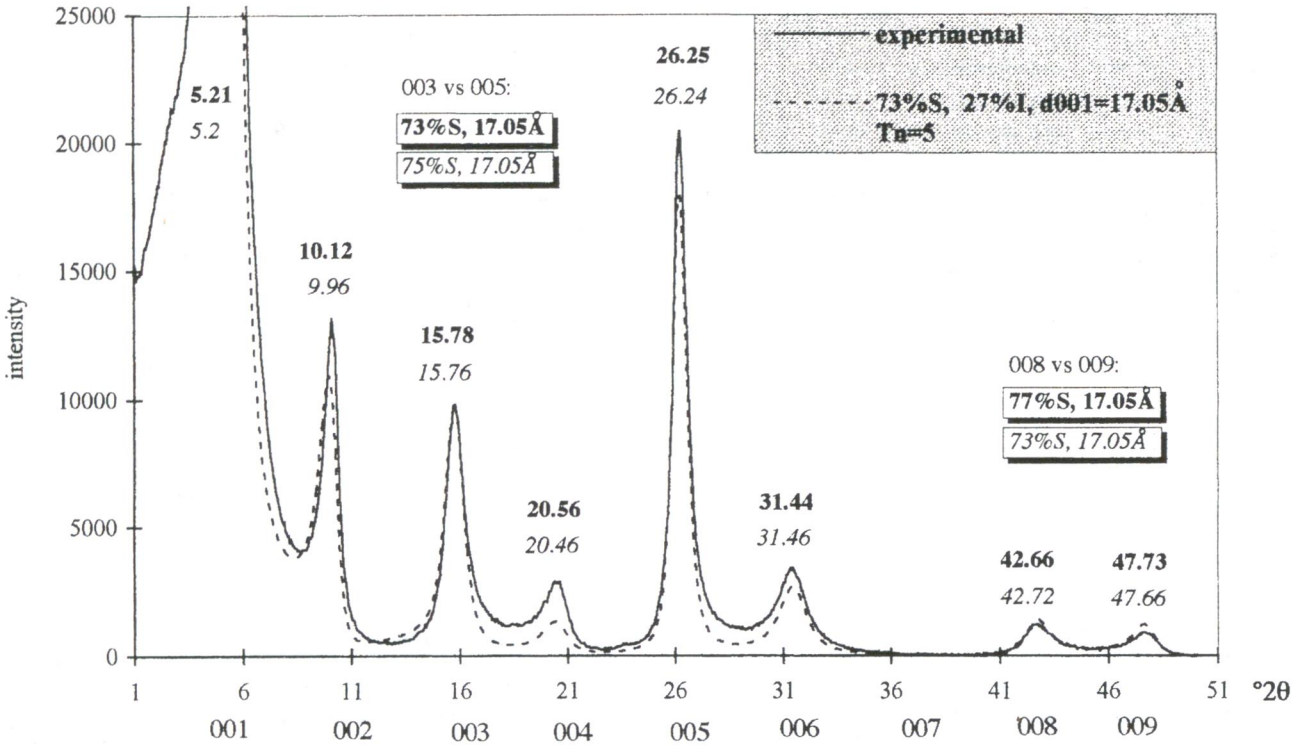


**Fig. 8.** Example of fitting the experimental (glycolated sample 2M3) XRD profile with the theoretical (calculated by NEWMOD) profile of randomly interstratified illite/smectite in complete 2 – 50° 2θ range. The calculation was performed for $T_n$= 5, using %S and $d_{001}$ of smectite measured from Fig. 5. Experimental peak positions are presented in bold, and calculated in italic. In boxes, measurements using 003 vs 005 and 008 vs 009 techniques for experimental and calculated patterns are shown in the same manner.

for 2M3 sample saturated with Na and Ca because, as it was demonstrated by Eberl et al. (1987), the 14 Å layers identified in Na-saturated samples expanded to 17 Å upon Ca exchange. We did not find, however, the differences in peak positions between XRD patterns of Na- and Ca-saturated 2M3 sample. Also the background characteristicts are the same. This result suggests that the presence of small amounts of 14 Å layers in mixed-layer minerals cannot account for the detected differences between estimates obtained using the two techniques. It was also found that bigger amounts of the third component, 10% of vermiculite or chlorite, can improve the fit significantly in 11 – 23° 2θ range, but makes it worse in 23 – 35° 2θ range. Also %S estimated from such pattern using our two techniques give unrealistically high differences in %S and $d_{001}$ of smectite, well above the readings from the experimental patterns (Fig. 9b). We conclude that the observed misfit and the differences between %S estimated using the two techniques are not due to mixed-layering. This conclusion is supported by the observation that similar misfit between 002 and 004 reflections is characteristic also for simulated pure smectites (unpublished). We suspect than that the observed features are caused by an error in estimating the $LpG^2$ function of smectite layers used in NEWMOD simulations: the effect expected to be very severe for 002 and 004 reflections, because they are located very close to zero values for the $LpG^2$ function. In these critical angular ranges, diffracted intensity is produced by multiplying the interference function by very small values of $LpG^2$: as a result, even a small error in estimating $LpG^2$ will result in big intensity differences.

## Conclusions

1. A lognormal model for crystal thickness distribution proposed by Drits et al.(in press), when applied in NEWMOD modelling of 00l reflections free of mixed-layering effects (dehydrated illite/ smectites), produces a much better fit than does an even model for the shape of experimental XRD patterns. Shifts of peak positions in the low-angle range, due to small crystal thickness, are controlled by the mean thickness rather than by the shape of the distribution.

2. The technique for measuring %S from the positions of low-angle reflections (Środoń 1980) has been refined by introducing the variation in mean crystal thickness with respect to %S documented by Drits et al. (in press). The refined technique tends to produce %S slightly lower (up to 7%) than the more sensitive high-angle technique, based on weak peaks with positions unaffected by crystal thickness. The measured difference in %S between the two techniques could

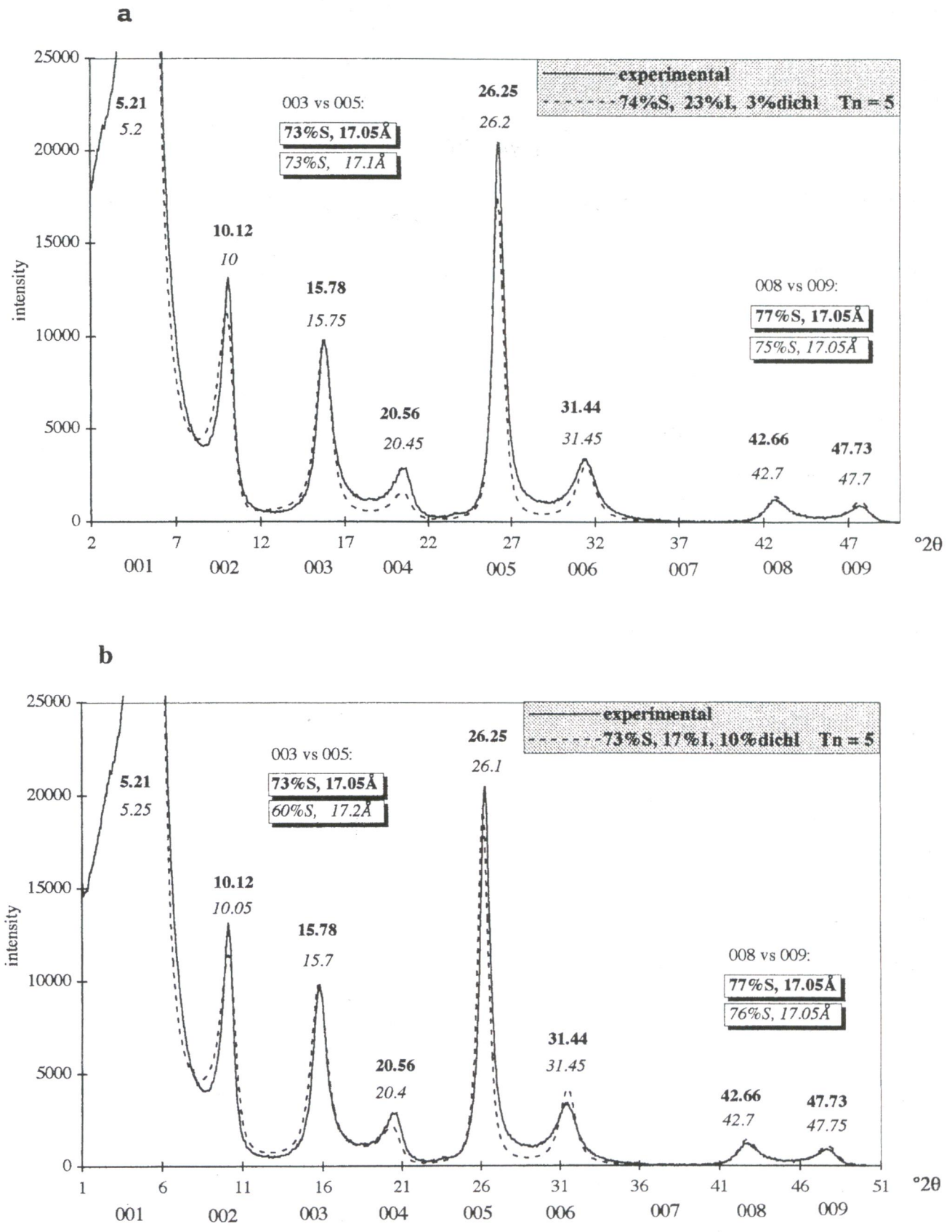


**Fig. 9.** An attempt to improve the fit from Fig. 8 using 3-component model: 3% (a) and 10% (b) of dioctahedral chlorite. The calculations were performed for $T_n = 5$. For explanations of symbols see Fig. 8.

not be explained by the presence of a third 14 Å component (vermiculite or chlorite).

3. A very good fit of peak positions and broadening is obtained if we simulate XRD pattern of illite/smectite in the complete 2 – 50° 2θ range using the values of %S and smectite $d_{001}$ estimated from one of the presented techniques and the lognormal distribution of the thickness of mixed-layer crystals which is appropriate for given %S. Minor differences are attributed to an error in estimating the $LpG^2$ factor of smectite used in NEWMOD calculations.

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