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The effect of particle size on apparent lattice spacings.

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Theoretical considerations suggest that particle-size effects can produce anomalous values for d_{00l} in certain structures. The effect is explained here in terms of the Laue interference function. Experimental results on very fine-grained mica correlate well with the theoretical relation between particle thickness and d_{00l}.

Under certain specific structural conditions, discrepancies may occur in measured d values because of the effects of very fine particle size. The existence of such effects has been noted by MacEwan, Ruiz Amil & Brown (1961) and Méring (1949). They conclude that the effects are most noticeable at low values of 2θ. More recently, Ross (1966) has considered the effect of particle thickness on the variations in d_{001}, d_{002}, and d_{003} for hypothetical thin crystallites of mica and montmorillonite. The present communication attempts to explain the cause of the particle size effect by the use of the interference function, and to correlate theoretical with observed discrepancies in d_{001} for clay-sized mica.

Theory

The treatment is applied to 001, 002, and 003 reflections from a randomly oriented crystalline aggregate whose crystallites are thin in the **c** direction, but large in the **a** and **b** directions.

The relative intensities of the basal reflections from such an aggregate (*e.g.* a mica) may be computed by the following expression (MacEwan *et al.*, 1961, p. 398):

$$I=\Xi|G|^2\Phi \tag{1}$$

where Ξ is the random powder Lorentz-polarization factor, $|G|^2$ is the squared modulus of the Fourier transform of the mica layer, and Φ is the interference function. For a one-dimensional case, Φ may be evaluated according to

$$\Phi=\frac{\sin^2(N\pi\zeta)}{\sin^2(\pi\zeta)}\,. \tag{2}$$

N is the number of reflecting elements (unit cells) in each array (crystallite), and ζ denotes the coordinate of a reciprocal lattice point. These relationships are developed and discussed by James (1965). Equations (1) and (2) can be used to compute a continuous intensity profile along **c***. In practice, this is rarely done. Instead, equation (1) is solved to give intensities at reciprocal lattice points. This procedure is sound because if N is large, Φ changes very rapidly with respect to ζ, and within the range of ζ in which Φ is significant, $\Xi|G|^2$ is practically constant.

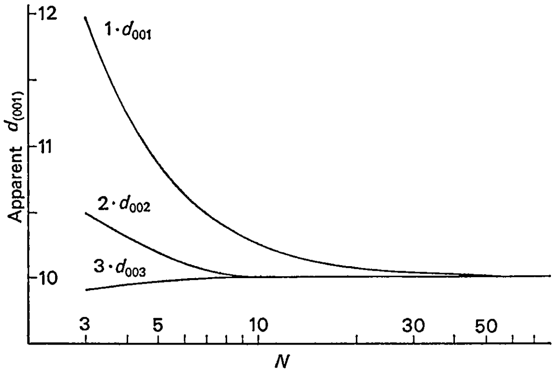

Fig. 1. Changes in apparent $d_{(001)}$ as a function of N. Actual $d_{(001)}=10{\cdot}000$ Å.

The breadths of the maxima in Φ increase as N is diminished. If N is sufficiently small, these maxima may be broadened enough to include a region of significant variation in $\Xi|G|^2$. Then, the intensity maximum is shifted toward the direction of increasing $\Xi|G|^2$. The magnitude of the shift is directly related to (1) the slope of $\Xi|G|^2$, and (2) the breadth of the Φ maximum. For complex crystals such as micas, the slope of $\Xi|G|^2$ will not be identical in regions of different $(00l)$ reciprocal lattice points. Consequently the shifts in the intensity maxima will be of different magnitudes and even in different directions. The resulting diffraction pattern will present an apparently irrational series of basal reflections.

Fig. 1 shows calculated values for apparent d_{001}, with respect to N. Computations were made for true $d_{001}=10{\cdot}000$ Å. The Fourier transform was evaluated with the use of silicate layer atomic parameters as given by Reynolds (1965), and assuming a potassium content of 0·8 atom per half unit cell. These conditions were selected in order to simulate better the composition of the clay micas (illites). It can be seen that the 001 and 002 peaks are shifted, at small N, toward higher d; the 003 is shifted toward lower d. Fig. 1 also shows that the spacing of the 001 reflection is far more sensitive to thickness effects than are the others. This sensitivity is manifested because the $\Xi|G|^2$ function rises steeply in this region of reciprocal space.

The results given above will not be precisely applicable to any given fine-grained illite aggregate. The curves of Fig. 1 would be modified by (1) variations in the details of structure, and hence in the form of G, (2) changes in the appropriate form of the Lorentz factor for different experimental conditions, and (3) the presence of a distribution of particle thicknesses, rather than a single one.

Experimental results

Diffraction patterns were obtained from a sample of micaceous fault gouge* that had been separated into a series of particle sizes by the use of an ultracentrifuge. The sample consists almost entirely of a dioctahedral aluminous mica; traces of chlorite were observed in the two coarsest particle-size fractions. In addition, one sample of muscovite was studied. This material was ground under water and the size range 20–10μ was separated for analysis.

Diffraction patterns were obtained with a General Electric XRD-5 diffractometer equipped with a copper tube and a nickel filter. A medium resolution Soller slit was used

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* The sample was collected 1·2 miles S 6° E of the southeast end of Lake Sunapee, New Hampshire.

in conjunction with detector and beam slits whose angular divergences are, respectively, 0·2° and 1°. All patterns were obtained at a goniometer scanning speed of 0·4° 2θ.min^{-1}.

Diffraction angles for the mica 001, 002, and 003 reflections were measured with respect to the same reflections for pyrophyllite, which was mixed with each of the mica particle-size fractions. The pyrophyllite initially had been standardized against quartz. Values for the mica reflections, converted to d, are given in Table 1, together with values for the quantity Δd_{001}, which expresses the discrepancy in d_{001} and is equal to $d_{001} - 3 \,.\, d_{003}$.

Table 1. *Spacings and pure diffraction breadths for basal reflections from micas of various particle sizes*

Stokes-Law equivalent spherical diameters*	d_{001}	d_{002}	d_{003}	Δd_{001}	β_{003}
Muscovite					(°2θ)
10 –20 µ	10·01	4·98	3·331	0·02	0·12
2 – 0·5 µ	10·00	4·97	3·323	0·03	0·38
0·5–0·2 µ	10·02	4·97	3·322	0·05	0·36
< 0·2 µ	10·04	4·98	3·319	0·08	0·43
< 0·03 µ	10·06	4·98	3·320	0·10	0·52
< 0·01 µ	10·14	4·97	3·314	0·20	0·83

* These particle-size values have little absolute significance. They are used here to facilitate correlation with the data of workers in the fields of clay mineralogy and soil science.

In order to determine the effective thickness of the crystallites in each of the size fractions, the breadths (in degrees 2θ) of the various mica 003 reflections (B) were read directly from the diffractometer profiles by measuring the peak breadths at half-height. A single crystal of muscovite was scanned, under the experimental conditions outlined above, and the breadth of its 003 reflection was taken as a measure of the instrumental broadening (b). Values for the pure diffraction breadth (β, Table 1) were computed according to an approximation given by Warren & Biscoe (1938) as

$$\beta = \sqrt{B^2 - b^2}\,.$$

Fig. 2 shows Δd_{001} plotted with respect to β_{003}. The bars about each point represent the error in establishing Δd_{001}, estimated from replicate analyses, and amounting to ± 0·02.

Discussion

The relations shown by Fig. 1 were used to compute Δd_{001} at different values of N. The Scherrer equation for line broadening was solved for β_{003} at each of these same values of N, assuming a shape factor of unity. The quantity Δd_{001} was plotted against β_{003}, for each N, providing the theoretical relation between Δd_{001} and β_{003} for mica. This relation is shown by the solid curve on Fig. 2. The experimentally measured values appear to show satisfactory agreement with the theory.

Conclusions

Experimental measurements tend to confirm the theoretical observation that very thin mica crystallites will show anomalously large values for d_{001}. The discrepancy may be significant for illitic clays. Therefore, the presence of a somewhat irrational series of basal reflections cannot be taken, in all cases, as evidence for interstratification. The possibility of a particle-size effect should also be considered.

Although the present work deals only with micas, the same theoretical considerations will apply to certain reflections from some other types of clay mineral. It seems that mean crystallite thickness must be considered as an independent variable, along with structure, composition, and interstratification, in the detailed interpretation of X-ray diffraction patterns from fine-grained clay minerals.

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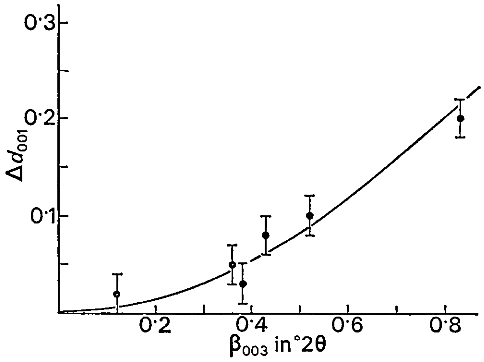

Fig. 2. Calculated curve for β_{003} with respect to Δd_{001}, and measured values for these quantities from the various mica size fractions.