PRECISION UNIT-CELL PARAMETER DETERMINATION OF LAYER SILICATES BY USE OF ELECTRON AND X-RAY DIFFRACTION POWDER TECHNIQUES

by

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EXTENDED ABSTRACT

THE USE of good quality X-ray and electron diffraction powder data in conjunction with modern least-squares analysis computer programs can yield very accurate lattice parameters for the various layer silicates. X-ray powder patterns of many of these minerals, however, contain unresolved doublet and triplet lines that prevent the unambiguous indexing of a large number of reflections, thus offering special problems for the least-squares program. Owing to the pseudohexagonal nature of the 1M and $2M_1$ mica structures, the following classes of reflections of approximately equal intensity overlap in the X-ray powder patterns: $2h0l$ and $h3h(\bar{l}-h)$; $0.6hl$ and $3h3h(\bar{h}\pm l)$. The following reflections overlap in the X-ray powder patterns of the $2M_2$ micas: $2h0l$ and $hh(\bar{l}-h)$; $0.2hl$ and $3hh(\bar{h}\pm l)$. Investigators in the past have been using the strong " 060 " reflection of the micas, chlorites etc. to determine the b unit-cell parameter. The 060 reflection overlaps the equally strong $33\bar{1}$ reflection of the 1M and $2M_1$ micas. A similar type of overlap occurs in the $2M_2$ micas and in the monoclinic and triclinic chlorites. This overlap makes it impossible to obtain a reliable value for b for the 1M, $2M_1$, and $2M_2$ micas from the so called " 060 " reflection unless the following two conditions are obeyed or very nearly obeyed: $b = a\sqrt{3}$ (or $a = b\sqrt{3}$) and $\beta = \cos^{-1}(-a/3c)$.

Because of the presence of a c-glide, the $2h0l$ reflections of the $2M_1$ and $2M_2$ micas are extinct if l is odd. Thus the $h3hl$ and hhl reflections of the $2M_1$ and $2M_2$ polymorphs respectively, will not overlap any $2h0l$ reflections when $h+l$ is odd. For the $2M_1$ micas the $h3hl$ reflections for which $h+l$ is odd are generally very weak or missing and thus probably will not appear in the X-ray powder pattern. On the other hand, the hhl reflections of the $2M_2$ micas where $h+l$ is odd may be quite strong. In fact, it is these reflections that will be the most useful for least-squares refinement.

The data suitable for use in the least-squares program that lie within the normal range of d spacings of the 1M and $2M_1$ mica powder patterns are the $00l$, $02l$, $04l$, $11l$, and $22l$ reflections. In addition to the $00l$ reflections, the $11l$, and $22l$ reflections, where $h+l$ is odd, are suitable for least-squares refinement of the $2M_2$ mica unit-cell parameters.

Electron diffraction powder patterns yield directly the true a and b unit-cell parameters of the layer silicates and thus serve as a complement to the X-ray powder method. Clay minerals orient on the specimen mount such that the (001) plane is perpendicular or nearly perpendicular to the electron beam. Owing to the thinness of the clay particles in the c^* direction the crystallites act as two-dimensional or pseudo–two-dimensional

† Publication authorized by the Director, U.S. Geological Survey.

https://doi.org/10.1346/CCMN.1964.0130111 Published online by Cambridge University Press

diffraction gratings to electrons. For such " thin crystal " diffraction gratings the reciprocal lattice nodes extend parallel to the electron beam an appreciable distance in reciprocal space. The diffraction geometry is thus slightly different from that of an ideal triperiodic grating. The expression relating the angle of diffraction ($2\theta'$) and the interplanar spacing d of powdered specimens acting as " thin crystal " diffraction gratings is $\lambda = d \sin 2\theta'$. It is shown that an unknown interplanar spacing (d_x) of such crystals can be evaluated to within 0.001 per cent from the relation $d_x = (d_s D_s \cos 2\theta_s)/(D_x \cos 2\theta_x)$, where d_s is the d spacing of the standard material, D_x and D_s are respectively the unknown and standard ring diameters of the electron diffraction powder patterns, $\theta_x = \sin^{-1}(\lambda/2d_x)$, and $\theta_s = \sin^{-1}(\lambda/2d_s)$. The d spacings (d_{hk}) given by an electron diffraction powder pattern of a layer silicate are related to the a and b unit-cell parameters by

$$d_{hk} = (h^2/a^2 + k^2/b^2)^{-\frac{1}{2}} \tag{1}$$

With the above expressions it is believed that d spacings may be evaluated from measurements of electron diffraction powder patterns taken with a high quality electron diffraction camera to an accuracy of a few parts in 10,000. These data may then be subjected to least-squares refinement to give very reliable a and b unit-cell edges. Such a refinement will be very useful in analysing layer silicates that give poor X-ray powder patterns. Full details of this study will be published elsewhere.