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CALCULATION OF ABSOLUTE DIFFRACTION INTENSITIES FOR MIXED-LAYERED CLAYS

Key Words—Computer calculation, Intensity, Mixed layer, X-ray powder diffraction.

Diffraction patterns for mixed-layered clays have been calculated by the computer methods described by Reynolds (1967), Reynolds and Hower (1970), Sakharov and Drits (1973), Cradwick (1975), Drits and Sakharov (1976), and Reynolds (1980). Versions of the programs used by Reynolds, called MOD-4 and MOD-8, have been informally distributed. The purpose of this note is to describe a few simple changes that can be made in these and similar programs that will put the calculated intensities on a correct relative basis for various clay types. Such calculated results can be used as calibration standards for semi-quantitative analysis of mixtures involving mixed-layered clays.

DISCUSSION

MOD-4 and MOD-8 compute the diffraction intensities by means of the Laue interference function expressed as a Fourier series (Reynolds, 1980). The treatment is identical to

$$I = \frac{|G|^2}{N} \frac{(1 + \cos^2 2\theta)}{\sin 2\theta \sin \theta} \frac{\sin^2(2\pi ND \sin \theta/\lambda)}{\sin^2(2\pi D \sin \theta/\lambda)}, \quad (1)$$

where N is the number of unit layers in coherent scattering array along c*, G is the amplitude of scattering in a plane normal to 001, the second quotient is the random powder Lorentz-polarization factor, and the sine-squared quotient is the Laue interference function. The arguments of the sine-squared quotient contain D, which is d001, θ, the diffraction angle, and λ, the wavelength. For this and other expressions described here, physical and instrumental constants have been disregarded. The "equals" sign is applicable for the desired results, but strictly, all equalities are in fact proportionalities.

The diffraction intensity, per unit of beam cross-sectional area, for a crystal so thin that absorption can be neglected, and uncorrected for polarization is given by (James, 1965, p. 38):

$$I(\epsilon) = |q|^2 \frac{\sin^2(2\pi ND \cos \theta_0 \epsilon/\lambda)}{\sin^2(2\pi D \cos \theta_0 \epsilon/\lambda)} \quad (2)$$

where θ_0 is the angle of a Bragg reflection and ϵ is the distance, in units of θ, on either side of the peak;

$$\theta = \theta_0 + \epsilon. \quad (3)$$

The quantity that concerns us here is q, the amplitude factor. It is derived (James, 1965, p. 35–36) by a Fresnel zone construction, and it gives the amplitude of scattering from a set of N parallel layers with structure factor G separated by D, and whose unit cells have volume V. Actually, James considered the number of unit cells per unit volume; here, the reciprocal of this quantity is termed V.

The result given by (James, 1965, p. 36) is

$$|q|^2 = \frac{|G|^2 D^2}{V^2 \sin^2 \theta}, \quad (4)$$

neglecting the wavelength and physical constants.

The calculation of absolute intensities requires the complete form of $|q|^2$, and terms preceding the interference function of Eq. (1) do not contain all the necessary quantities. The correct form for $|q|^2$ requires the development of James' formulation so that it applies to an infinitely thick crystalline aggregate whose diffraction intensities are corrected for polarization and the powder-ring distribution factor. First, however, proof is given that the interference functions in Eqs. (1) and (2) are essentially identical. The proof requires that

$$\sin^2(2\pi D \cos(\theta_0)\epsilon/\lambda) = \sin^2(2\pi D \sin\theta/\lambda). \quad (5)$$

The right side of Eq. (5) can be written (see Eq. (3)) as $\sin^2(2\pi D \sin(\theta_0 + \epsilon)/\lambda)$, and by identity, $\sin(\theta + \epsilon) = \sin\theta_0 \cdot \cos\epsilon + \cos\theta_0 \sin\epsilon$. The increment ϵ is always very small because diffraction is restricted to a small angular range about θ_0, consequently, $\cos\epsilon \cong 1$ and $\sin\epsilon \cong \epsilon$. Thus,

$$\sin^2(2\pi D \sin\theta/\lambda) = \sin^2(2\pi D \sin\theta_0/\lambda + 2\pi D \cos\theta_0 \epsilon/\lambda). \quad (6)$$

The Bragg law is given by $n\lambda = 2D \sin\theta_0$, or $n = 2D \cdot \sin\theta_0/\lambda$; substituting this into the right side of Eq. (6) provides the result, $\sin^2(n\pi + 2\pi D \cos\theta_0\epsilon/\lambda)$.

The term $n\pi$ represents phase shifts of zero or 180°, and either added to the angle $2\pi D \cos\theta_0\epsilon/\lambda$ produces angles whose sines have identical magnitudes but opposite signs. The sign is of no consequence because the desired quantity is given by the sign squared, thus the term $n\pi$ may be disregarded, and the result is $\sin^2(2\pi D \cos\theta_0\epsilon/\lambda)$ which is identical to the left side of Eq. (5), constituting proof of the near identity given by Eq. (5).

Return now to the development of the intensity factor $|q|^2$ or simply q^2 if the crystal layers are centrosymmetric or projection to c*. Intensity is proportional to the volume irradiated which can be separated from Eq. (4) as follows:

$$q^2 = \frac{G^2 D}{NV^2 \sin\theta}(1/\sin\theta)(ND). \quad (7)$$

The terms $1/\sin\theta$ and ND are proportional, respectively, to the area and the depth of irradiation. ND can be replaced by $\sin\theta/(\mu^*\rho)$ for a crystalline aggregate diffracting in the reflection mode, if the aggregate is so thick that absorption within it is complete (see Brindley, 1961, for the introduction of ρ). Here, μ^* is the mass absorption coefficient and ρ is the density of the mineral. If the area and depth terms are multiplied, the result is $1/(\mu^*\rho)$, proving that the absorption correction is angle independent for the assumed flat-specimen reflection geometry (Klug and Alexander, 1974, p. 486).

Two additional factors are necessary for the treatment of diffraction intensity from a thick slab of powder, the polarization factor $(1 + \cos^2 2\theta)$, and the powder ring distribution portion of the Lorentz factor which is $1/\sin\theta$ for random orientation. Putting this all together yields

$$I = \frac{G^2 D}{NV^2 \mu^* \rho}\left(\frac{1 + \cos^2 2\theta}{\sin^2\theta}\right)\Phi \quad (8)$$

where Φ is the interference function (Eq. (1)).

MOD-4 and MOD-8 need to be modified as follows: (1) Replace $\sin 2\theta \sin\theta$ in the denominator of the Lorentz-polarization factor by $\sin^2\theta$. (2) Multiply the calculated intensities by $D/(V^2\rho)$. The programs presently incorporate the correct values for N or mean N. The mass absorption coefficient can be neglected if it is understood that the results apply, from two successive computer runs, to a 50/50 mixture by weight of the two clay types involved. Of course, at that point, the calculated intensities can be scaled linearly to any other weight ratio. Values for V and ρ are simple weighted means of the end-member values. Data on V can be found in Brindley and Brown (1980), and ρ is best calculated from the molecular weight and V (see Buerger, 1960, p. 243).

[1] In this and other equations taken from James (1965), the symbols have been changed to make them consistent with the treatment given by Reynolds (1980).

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COMMENTS

Computer methods have had good success in accurately simulating diffraction patterns for mixed-layered clays, in part because peak positions are insensitive to variations in G, the layer transform. Correct intensities are another matter. Small changes in atomic positions or variations in K and Fe content will change considerably the intensities of some reflections. Consequently, the use of these or other similar computer methods for quantitative standardization should be considered to be at best semiquantitative.

Certain precautions should be taken to optimize accuracy. The strongest reflections in the calculated profiles, *after* extraction of the Lorentz-polarization factor, are the least sensitive to chemical and structural variations, and these are the best to use. There are uncertainties in the Lorentz factor at very low 2θ for highly oriented samples and for instruments with poor soller slit collimation. Consequently, analytical specimens should not be extremely well oriented, the instrument should incorporate 2° or finer soller slits on the beam and detector sides, and the use of low-angle peaks (below 10° for CuKα) should be avoided insofar as that is possible. Finally, the careful selection of sample length and beam-slit relations is necessary for correct low-angle intensities, particularly when calculated results are to be compared with experimental patterns obtained from large-radius goniometers such as the Siemens D-500.

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