

NOTE ON THE VARIANCE IN X-RAY QUARTZ-POWDER
DIFFRACTION PATTERNS

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Incidental to continuing Debye-Scherrer-method investigations of crystalline structure as part of the study of Electrosmosis¹ which one of us (EFP) is making, there was occasion to note the variance in reflection patterns from the same powdered quartz^{2,3} sample using a rotating thread-like target and a stationary wedge-shaped target.

Material for the targets was ground up in a mortar. Powder for the thread, an amount that could be scooped up on the end of a needle, was bound by approximately an equal amount of adhesive⁴ of toluene and ethyl-cellulose; then, by rolling between two glass plates, it was drawn into a thin rod .003-.005 inches in diameter. The wedge-shaped target was formed, without binder, by packing in a small cradle holder and mounted such that the primary beam grazed the edge. Photographs were made with a North American Philips Company x-ray diffraction unit in a cylindrical camera 114.59 mm. in diameter. The weighted average wavelength of K_{α_1} and K_{α_2} copper radiation and nickel filter were employed, the tube voltage and current being 35 KV and 25 ma. respectively; the exposure time was 2.3 hours and the temperature 21.5° C.

By independent methods, several authors⁵⁻⁹ have obtained expressions for the intensity of x-ray reflection; most of these are in agreement with each other. Compton⁹ has derived formulas which are applicable to the following considerations:

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¹ Preece, E. F., *Highway Research Board Proceedings*, **27**, 384-417 (1947).

² Many photographs of powdered soil samples displayed the fan-shaped convergence of Fig. 2C. By elimination it appeared that the effect was due to the quartz component.

³ Quartz occurs both as large crystals and as microscopic grains, in both cases apparently with identically the same crystal structure of either primary or secondary radiation.

⁴ Dr. Christ and co-workers, U. S. Geological Survey, suggested a mixture in ratio of 5 grams ethyl-cellulose to 100 cc. of toluene; authors used 7 grams and 100 cc.

⁵ Debye, P., *Ann. d. Physik*, **43**, 49 (1914).

⁶ Bragg, W. L., James and Bosanquet, *Phil. Mag.*, **41**, 309 (1921).

⁷ Greenwood, G., *Phil. Mag.*, (7), **3**, 936 (1927).

⁸ Compton, A. H., *Phys. Rev.*, **9**, 29 (1917).

⁹ Compton, A. H., *X-Rays and Electrons*.

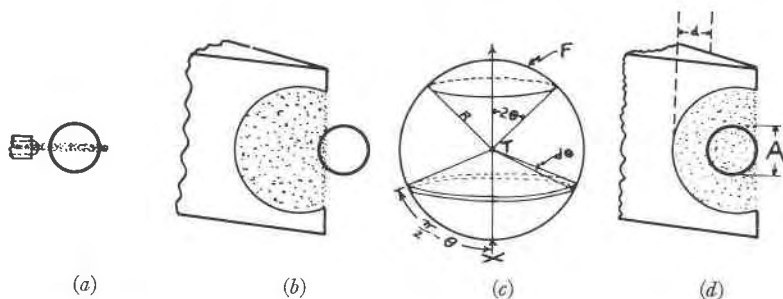


FIG. 1. Relative size and position of target to incident beam of cross-sectional area A : (a) rotating "thread," (b) stationary wedge barely grazed by incident beam, (c) relationship of incident beam X , target T , diffracted rays R , and film F , (d) same wedge as in b intercepting full x -ray beam.

The thread (Fig. 1a) is a small cylindrical mass of rotating crystals whose orientations have a continuous random distribution and whose volume is considered so small that we can neglect absorption of the x rays which bathe it. A small correction may be made for absorption in the binder—cellulose is an organic material consisting of atoms of low atomic numbers and yields very faint, ill-defined x -ray diffraction patterns. This proceeds as for a powder containing ingredients of different absorption coefficients.¹⁰ For a given angle of diffraction the intensity distribution in the resulting halo (Fig. 2a) of any cone whose axis is the direction of the incident beam will be uniform. The total energy W reflected by crystals rotated through angle θ with uniform velocity ω is proportional to the volume Δv of the crystal.

$$W = Q\Delta v I_0 = I_0 \int P(\theta) d\theta$$

I_0 is the incident energy in the primary x -ray beam and Q is given by

$$Q = \frac{N^2 \tau^3}{2u} F^2 \frac{e^4}{m^2 c^4} \frac{1 + \cos^2 2\theta}{\sin 2\theta}$$

where N is the number of atoms per unit volume, u the effective absorption coefficient of the crystal, τ the wavelength of the x rays used, m the mass of the electron, e the charge on the electron, c the velocity of light, $1 + \cos^2 2\theta$ the polarization factor, and F is termed the structure factor and is defined by the equation

$$F = Z \int_{-a}^a P(z) \cos\left(\frac{4\pi z}{\tau} \sin \theta\right) dz$$

¹⁰ Bradley, A. J., *Proc. Phys. Soc.*, **47**, 879 (1935).

where z is the number of electrons in the atom, a is the maximum possible distance of an electron from its atomic layer and $P(z)$ represents the probability that an electron will be at a distance z and $(z+dz)$ from the mid-plane of the layer of atoms to which it belongs. In the integral, $P(\theta)I_0$ is radiation reflected in direction θ by a particle.

When the incident beam just grazes a stationary wedge (Fig. 1*b*), absorption is again negligible and the normals to the crystal planes which contribute to a halo all lie close to a cone whose semi-vertical angle from X is $(\pi/2) - \theta$ (Fig. 1*c*), or say between two cones whose semi-vertical angles are $(\pi/2) - \theta$ and $(\pi/2) - (\theta + d\theta)$. For random distribution of orientations the possibility of a normal lying between these two cones is equal to the ratio of the area cut off between the two cones from the surface of a sphere with T as center to the whole surface area or $(1/2) \cos \theta d\theta$. Considering N particles in all, a number $(1/2)N \cos \theta d\theta$ will have their normals lying within the given range, and if $\overline{P(\theta)}$ is the average reflecting power of a particle, the total energy reflected into the halo (Fig. 2*b*) will be

$$\frac{1}{2}NI_0 \cos \theta d\theta \overline{P(\theta)}$$

or integrating over all values of θ ,

$$P = \frac{1}{2}NI_0 \cos \theta \int \overline{P(\theta)} d\theta$$

where for the small range of effective angles in the vicinity of θ_0 , $\cos \theta$ is taken as a constant and equal to $\cos \theta_0$ in the integration. From above

$$P(\theta)d\theta = Q\Delta v$$

then

$$P = \frac{1}{2}NI_0 \cos \theta_0 \overline{dv}$$

where \overline{dv} is the average volume of a particle. Hence, $N\overline{dv}$ is the total volume V of the powder, and

$$\frac{P}{I_0} = \frac{1}{2} \cos \theta_0 QV.$$

Sets of planes with different crystallographic indices, having the same spacing reflect into the same halo. If there are n such sets, then

$$\frac{P}{I_0} = \frac{n}{2} \cos \theta_0 QV.$$

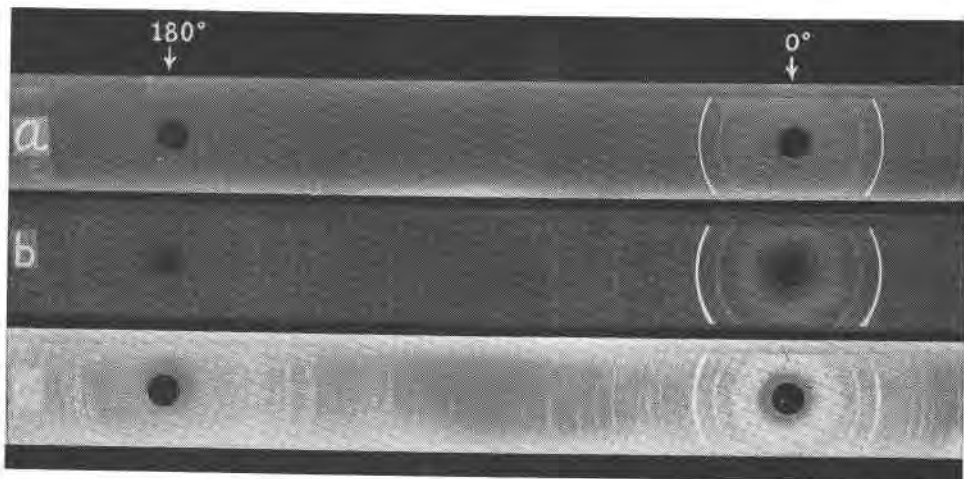


FIG. 2. Quartz-powder photograph: (a) rotating thread, (b) grazed stationary wedge (c) wedge interception of all incident radiation

In the final consideration (Fig. 1*d*) the wedge is mounted such that the rays are perpendicular to a plane bisecting the wedge angle and involve a greater volume of particles with the full incident beam of cross-sectional area A . The total volume irradiated is $(\rho'/\rho)(d/2)A$ where ρ' and ρ are the densities of the powder and the crystal in bulk respectively; d is thickness through wedge. There is an optimum thickness in the wedge where the energy falling into a halo is a maximum when d equals $1/u$ where u is the linear absorption coefficient of a section for the radiation.

The relative intensities of the lines (Fig. 2*c*), considering that full beam energy is involved, appear influenced by the absorption of the x rays. The fan-shaped convergence with disappearing small illumination spots, absent for the first mounting, appears strongly. This turbulent distribution of interference gives the deception of order effect which does not exist.

The K_{α} doublet is most conveniently observed in the region where 2θ is nearly 180° (Figs. 2*b* and 2*c*) since dispersion is very high in this region and the components have a wide angular separation. The apparent reversal of the stronger K_{α_1} line with the weaker K_{α_2} line is characteristic of back reflection patterns.¹¹

The interest of Dr. J. C. Hubbard, to whom one of us (AFG) is indebted for stimulating discussions, is gratefully acknowledged by the authors.

¹¹ Clark, G. L., *Applied X-Rays*.