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AN EXPERIMENTAL DETERMINATION OF THE EFFECT OF POWDER
SAMPLE POROSITY ON X-RAY INTEGRATED INTENSITIES

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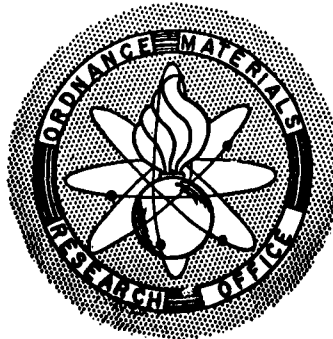
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ABSTRACT

Some measurements are presented which support a simple
derivation for the effect of porosity on the integrated inten-
sity of Bragg peaks in powders. A practical method of correct-
ing for porosity is presented which makes use of fluorescent
radiation from the sample.

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It is the purpose of this note to underscore the fact that porosity
(or surface roughness) can give rise to large errors in X-ray intensity
measurements on powders and to propose a simple semi-empirical expression
for estimating the effect of porosity and a practical method for correcting
for it.

If one is measuring the Bragg peaks from an infinitely thick powder
sample in symmetrical reflection then the integrated intensity in absence
of extinction is ordinarily taken to be proportional to $Q/2\mu$ (James 1954,
p. 51) where μ is the linear absorption coefficient of the bulk material
and Q is the integrated reflecting power per unit volume of a single crystal-
lite. This expression is valid either for a powder sample whose apparent
density equals the true density of the bulk material or for a powder sample
whose particle size is so small that the X-ray traverses a great many par-
ticles. However even for a particle size as small as a few microns the
absorption coefficient for elements of $Z > 25$ is so high as to limit the
depth of penetration of X-rays to only a few particles. Thus we can expect
that the X-rays will traverse a statistical distribution of path lengths on
entering and leaving a typical powder sample. On the average, though, the
emergent path lengths are greater than the path lengths on entering. Since
the Bragg intensity is proportional to the amount of sample traversed by
the X-rays and the absorption of X-rays is exponential there is a different
averaging for the two competing processes. It turns out that this reduces
the intensity from that expected from $Q/2\mu$ by as much as 20% in typical
cases encountered in X-ray diffraction.

We have calculated the integrated intensity in infinitely thick powder
samples in symmetrical reflection on the simple assumption that the X-rays

encounter a distribution in emergent path lengths exp $[-\epsilon|\Delta|n/(1-\alpha)]$ where
n is the average number of particles traversed by the X-ray, $1+\Delta$ the cor-
rection to the emergent path length, ϵ an adjustable parameter and α the
ratio of the average path length in the powder sample to the path length in
a bulk sample, i.e., the ratio of the apparent density of the powder to the
true density of the solid. As is expected such a distribution function be-
comes narrower as either the apparent density or n increases and becomes a
delta funtion when $\alpha = 1$. The reason for the longer emergent path lengths
can be seen in Fig. 1 where an entering X-ray is seen to penetrate quite
deeply due to voids and thus cannot easily leave. If the reverse ray were
equally intense (reverse the arrows in Fig. 1), there would be no porosity
effect but such a reversed ray would have been scattered or absorbed before
reaching this depth.

If we let d equal the average particle size then n $\widetilde{=}$ $1/\mu d$ and a straight-
forward integration yields (x is the depth from the surface)

$$I \propto Q \int_o^\infty dx \int_r^\infty \frac{\alpha}{\sin\theta} \exp\left[\frac{-2\mu\alpha x(1+\Delta)}{\sin\theta}\right]\exp\left[\frac{-\epsilon n|\Delta|}{1-\alpha}\right]d\Delta \bigg/ \int_o^\infty \exp\left[\frac{-\epsilon n|\Delta|}{1-\alpha}\right]d\Delta$$

$$I \propto \frac{Q}{2\mu} \ 1 - \left[\frac{(1-\alpha)\mu d}{2\epsilon}\right] \qquad (1)$$

valid for $\mu d < 1$

showing that the intensity decreases from that expected by the bulk sample,
$Q/2\mu$. In the limit as either μ or d approaches zero or α approaches unity
the intensity for the bulk sample is realized.

In Fig. 2 are the results of integrated intensity measurements of the
111 and 200 reflections taken from ten micron size aluminum powder compressed
into briquets under varying pressures so as to vary the density from
1.28 gm/cm^3 to 1.95 gm/cm^3 (true density 2.70 gm/cm^3). At MoK$\alpha\lambda$ ($\mu = 13.5$/cm)

the X-rays penetrate about 100 particles and the intensity of the (111) peak appears independent of packing density. At Cr Kαλ(μ = 400/cm) the X-rays only penetrate a few particles and both the (111) and (200) peaks show intensity loss in the low density samples. The best fit of eq. 1 (solid lines in Fig. 2) is obtained by adjusting the parameter ϵ so that $\epsilon \overset{\sim}{=} 1.0$.

Using this value of the parameter ϵ, Fig. 3 shows the results of comparing eq. 1 with intensity measurements of the 110 reflection taken from five micron carbonyl iron powder at Ag Kαλ(μ = 143/cm), Mo Kαλ(μ = 295/cm), Cr Kαλ(μ = 906/cm) and Cu Kαλ(μ = 2500/cm). For Ag Kαλ the X-rays penetrate about fifteen particles while for Cu Kαλ only one to two particles are penetrated. After making a small correction for preferred orientation in the high density samples, the good agreement with eq. 1 (solid lines) over a wide range of density and absorption coefficients leads us to believe that eq. 1 is useful in estimating the porosity effect.

If the sample is caused to fluoresce be the incident radiation then a measurement of the fluorescent intensity relative to the fluorescent intensity from a bulk polished sample enables one to make a direct estimate of the effect of porosity on the Bragg intensity without requiring a knowledge of α or d. Employing the same formulation that led to eq. 1 and replacing μ by $(\mu + \mu^*)/2$ we find that the integrated intensity of the Bragg peak is reduced by a factor R given by

$$R \overset{\sim}{=} 1 - \frac{(\mu+\mu^*)(1-R^*)}{2\mu^*} \tag{2}$$

which is independent of the distribution function selected and where R^* is the ratio of the fluorescent intensity from the porous sample to that from a polished bulk sample, μ the linear absorption coefficient of the incident radiation and μ^* the average linear absorption coefficient of the fluorescent radiation (FeKαλ and FeKβλ in our measurement).

In Fig. 4 the measured values of R for Cu Kαλ (Fig. 3) are plotted against the right side of eq. 2 utilizing measured values of R*. The agreement is good to < 10% and leads us to suggest the use of eq. 2 as a practical method for estimating the correction for porosity, particularly when the correction is small.

There have been previous considerations of the effect of porosity (Taylor (1944), Brentano (1935), Schäfer (1933), Brindley (1945), Rusterholz (1931), de Wolff (1947), Wilchinsky (1951). Several of the authors have given elaborate derivations which in the main agree with eq. 1 (except for some differences in the power of the term $(1-\alpha)$ depending on the model) but none of the expressions yield any better representation of the data in Figs. 2 and 3 than our simply derived expression. (An examination of powder particles under a microscope indicates that their irregular shapes are hardly amenable to a sophisticated calculation). Wilchinsky has made some measurements on powders of particle size $0.3 < \mu d < 16$ principally to show that a treatment such as in eq. 1 is not valid for $\mu d \gg 1$.[†] Batterman, Chipman and DeMarco (1961) have utilized the fluorescent intensity of their compressed powder samples to eliminate porosity effects by selecting a sample whose fluorescent intensity equalled that of a solid specimen. Figure 4 and eq. 2 lend support to their procedure.

[†] *In such a case it may be reasonable to replace μd by μd^* where d^* is an effective depth of penetration into the particle. This should not affect eq. 2, though, since it is independent of the distribution function.*

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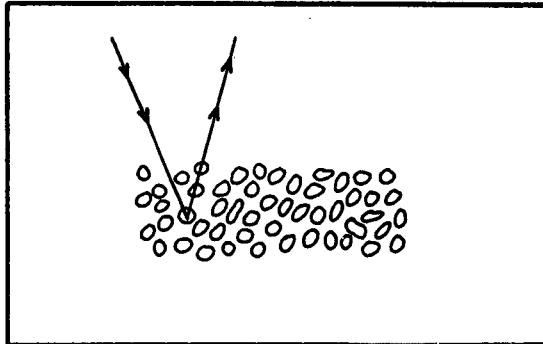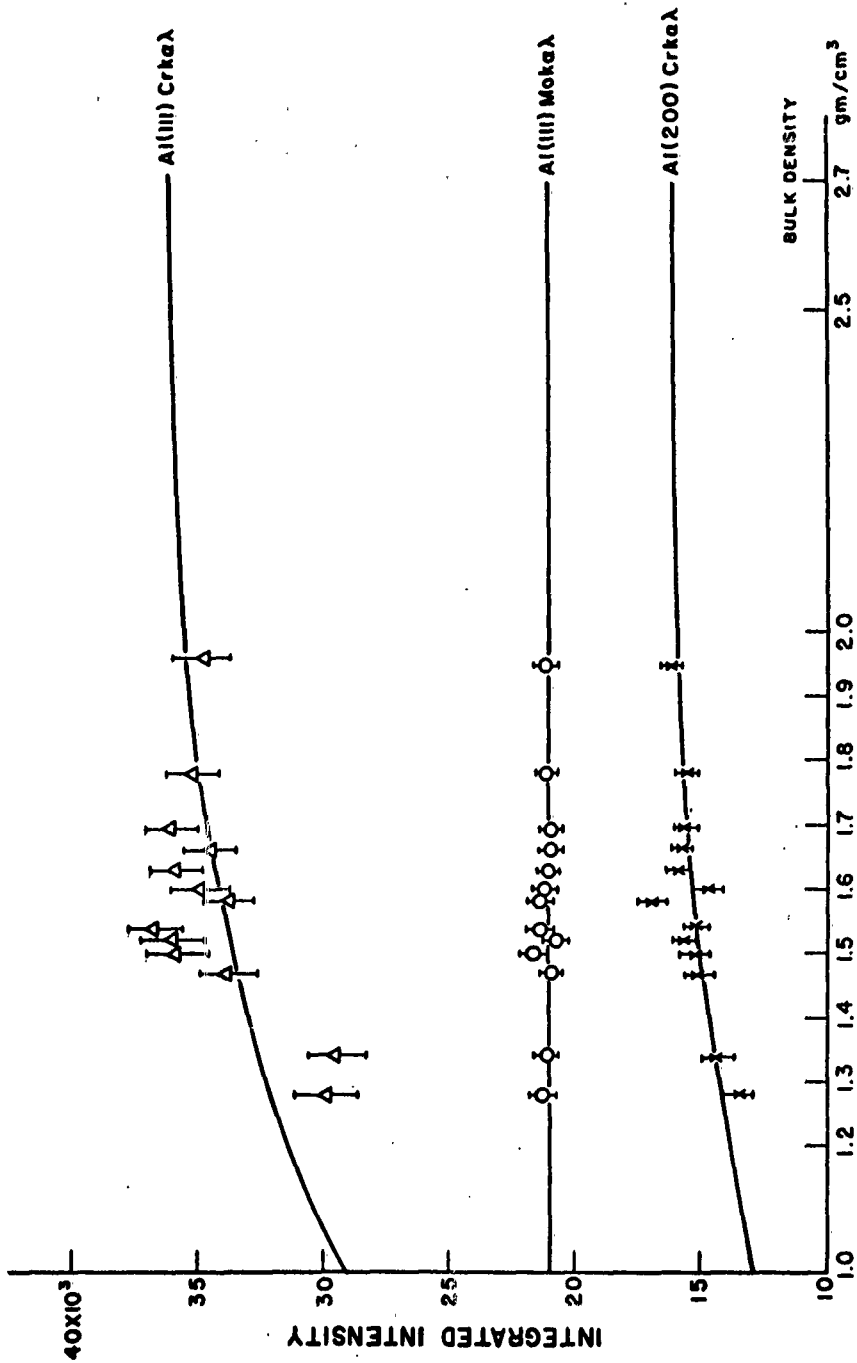
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Fig. 1. A schematic sketch showing that, on the average, emergent
path lengths in the sample are greater than entering path
lengths since a certain fraction of X-rays can enter quite
deeply through voids.

Fig. 2. The integrated intensity of the Al 111 peak at Mo Kα and the Al 111 and 200 peaks at Cr Kα as a function of the apparent density of the powder sample. The solid curves are an empirical fit of eq. 1 for $\epsilon \approx 1.0$ and d (measured) $\approx 10^{-3}$cm.
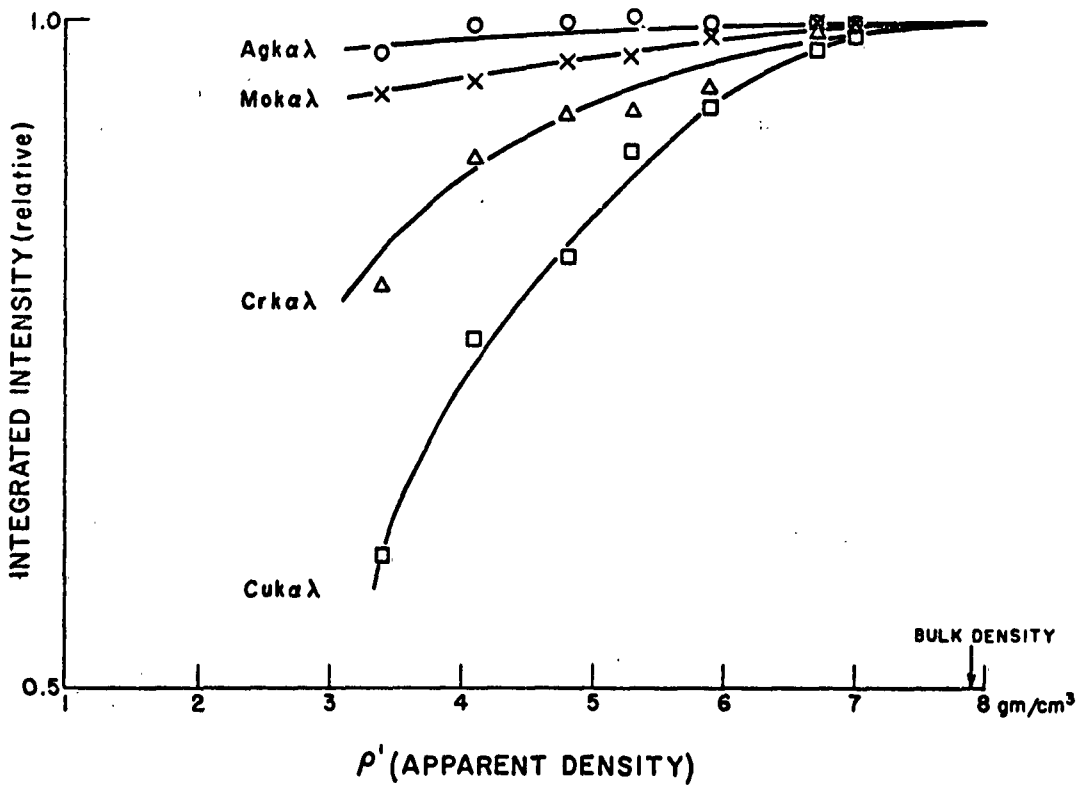
Fig. 3.   The integrated intensity of the Fe 110 peak at Ag Kα, Mo Kα,
           Cr Kα and Cu Kα wave lengths as a function of apparent density
           of the 5 micron carbonyl Fe powder samples.   The solid curves
           are determined from eq. 1 (ϵ = 1.0).

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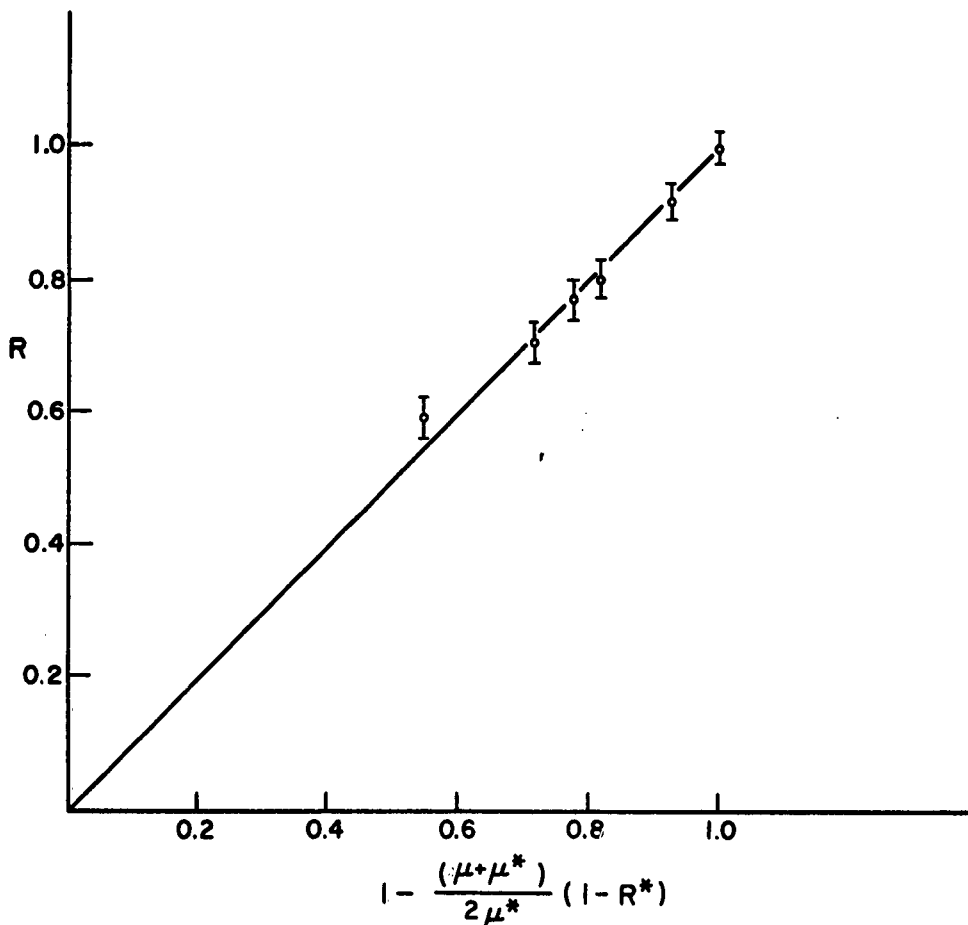
Fig. 4. The ratio of the integrated intensity of the 110 Fe peak relative to a powder sample with no porosity (extrapolated) versus the argument in eq. 2, taken with Cu Kαλ. R* is the ratio of the fluorescent intensity of the powder sample to the fluorescent intensity of a solid polished sample. If the fluorescent intensity of a powder sample equals the fluorescent intensity of a solid specimen of the same material then porosity effects are absent.

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