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Measurement of particle absorption by X-ray fluorescence.

By P. M. de Wolff,* *Philips Laboratories, Irvington-on-Hudson, N. Y., U.S.A.*

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The intensity, P, of secondary X-rays (either scattered or fluorescent) from a powder specimen will depend on particle size on account of absorption†. With vanishing particle size (chemical composition, geometry etc. being kept equal) a limit P_0 is approached, and P/P_0 is a convenient measure of this 'particle absorption' effect (Wilchinsky, 1951).

It should be noted that this definition is unambiguous only in the case of a sample with a flat surface used in reflection (that is, with the primary beam impinging on this surface at an angle α smaller than the deviation angle 2φ, so that the secondary beam emerges from the same surface). In the transmission case, for instance, one has to define exactly what 'constant thickness' means with varying particle size. In the following, only the dimension-free reflection case is treated.

It is possible to measure P/P_0 in the way indicated by the definition. Wilchinsky (1951) has actually performed diffraction experiments using graded fractions of iron and tungsten powder, in order to test his theory of the effect. Such experiments are extremely delicate, so that the description presently to be given of a less direct but much easier method was thought worth while. This method brings out a new aspect of particle absorption, namely its angular dependence, which has not been measured before nor predicted from theory (except by Wilchinsky, in so far as his theory presents a singularity for $\varphi = 90°$ whereas φ does not otherwise enter in his formulas for P/P_0).

An ordinary diffractometer of the Bragg–Brentano type can be used without essential modifications.

The sample is mounted as usual, but filters, electronic discriminators etc. are so adjusted that only fluorescent radiation is registered.

A run taken under these conditions—but with the usual 2:1 sample drive—should yield a constant intensity level for a sample free from particle absorption, such as a single-phase solid metal. In other words, the function $P_0(\varphi)$ is a constant. This is because fluorescence is isotropic, and because the geometrical intensity factor for fluorescence, like that for scattering, does not contain the goniometer angle φ. Therefore, any angular dependance of particle absorption in a powder sample will show up, without any distortion, in the record of a similar run with this sample.

From $P(\varphi)$ as a function of the goniometer angle φ, the particle absorption factor $P(\varphi)/P_0$ can then be derived, provided it has been determined for a single value of φ. This can be achieved in two ways:

1. Directly, that is by measuring under the same conditions the intensity emitted by a specimen of the same chemical composition but sufficiently fine-grained to ensure absence of particle absorption.
2. For particles consisting of a single phase: by extrapolating $P(\varphi)$ towards $\varphi = 90°$ and making use of the relation
$$P(90°) = P_0 ,$$
that is, for $\varphi = 90°$ the particle absorption effect vanishes. This relation is valid only for monophase particles embedded in a transparent binder (or air); it is not restricted to the model for which Wilchinsky (1951) derived it, but is easily shown to obtain independently from particle form and configuration, as well as from particle size distribution.

As a matter of fact, for $\varphi = 90°$ primary rays towards a given volume element coincide with the secondary rays emerging from it. Only in that case can the combined absorption of both be expressed in a single parameter, namely the total length intercepted by particles on the path of radiation directed to the volume element. Moreover, this parameter plays exactly the same role as the depth beneath the surface of a solid specimen, so that the integrated results are identical.

Experiments have been performed with copper in the form of solid metal as well as filings. Fluorescent Cu K radiation was excited by irradiating the sample in a Norelco diffractometer, using a molybdenum anode. It was recorded selectively by using a scintillation crystal and pulse-height discrimination, which cut off Mo K and most of the white scattered radiation. What remained of the latter was suppressed by putting an iron filter before, and a nickel filter behind the specimen. In this way the curves of Fig. 1 have been obtained (a special extra-fast goniometer drive of 15°/min. was provisionally made for this experiment). The curve from the solid sample shows P_0 to be constant, as predicted. The other three curves indicate a general S-shape, strongly

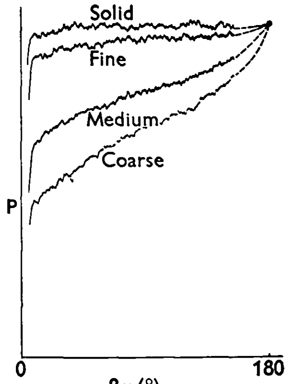

Fig. 1. Fluorescent Cu K intensity P from copper samples irradiated with Mo K and white radiation, recorded as a function of the goniometer angle 2φ.

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† Unlike Wilchinsky, we shall assume that P has been corrected for all other effects dependent on particle size, such as extinction.

rounding off the discontinuity in Wilchinsky's theory but converging in a most satisfactory way to a common intersection at $\varphi = 90°$ and at the level of the curve for the solid sample.

Many questions, such as the dependance of the effect thus measured on wavelength of primary and secondary radiation (important if the result is to be used for diffraction), the analogous effect for specimens used in transmission, influence of a non-transparent binder etc., can be studied conveniently by using fluorescence. It is hoped that continued research by the present empirical method will some time give a sufficiently clear picture of particle absorption to enable one to make a reliable estimate of the effect in quantitative X-ray work.

The extra-fast goniometer drive was constructed by K. Lowitzsch. His assistance, as well as helpful discussions with Dr W. Parrish and several colleagues at the Philips laboratories, are hereby gratefully acknowledged.

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Polymorphim in lead metaniobate.*

By M. H. Francombe, *Research Laboratories of The General Electric Company Limited, Wembley, England*

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X-ray diffraction powder studies of sintered ceramic specimens of lead metaniobate ($PbNb_2O_6$) have shown that this compound can adopt a structural form distinct from the orthorhombic, ferroelectric structure reported by Goodman (1953). This second structure is produced in specimens which have been fired in air at temperatures near 1200° C. Ceramic preparations made under these conditions are light fawn in colour and show no evidence of ferroelectric behaviour.

From 19 cm. camera X-ray powder photographs the crystal structure of the new polymorphic form is seen to be a deformed perovskite type. The deformation is rhombohedral, the simplest structure cell possessing the dimensions

$$a_R = 6{\cdot}206\ \text{Å},\ \alpha_R = 58°\ 18'.$$

To display more clearly the relationship to the idealized perovskite structure a larger, pseudo-cubic cell may be chosen with dimensions

$$a'_R = 8{\cdot}664\ \text{Å},\ \alpha'_R = 88°\ 30'.$$

This can be visualized as consisting of eight distorted simple perovskite-type cells. In ⟨100⟩ directions, referred to the multiple-type cell, Pb^{2+} ions alternate with vacancies on the *A* sites, and thus {222} planes contain only oxygen ions and unfilled Pb^{2+} sites.

Interplanar spacings, *hkl* indices (referred to hexagonal axes) and peak intensity values (derived from powder photograph microdensitometer data and from data obtained with a Philips X-ray diffractometer) are listed in Table 1.

Turning now to the orthorhombic, ferroelectric lead metaniobate reported by Goodman (1953), we have prepared ceramic samples of this form by using firing temperatures in excess of 1250° C. By fusing these products in platinum boats at about 1350° C. columnar crystals of up to 2–3 mm. in length were obtained. Crystals thus prepared in air and in a PbO atmosphere

Table 1. *X-ray powder diffraction data for rhombohedral form of* $PbNb_2O_6$

(19 cm. camera, Cu $K\alpha$ radiation)

hkl	*d* (Å)	*I*	*hkl*	*d* (Å)	*I*	*hkl*	*d* (Å)	*I*
200	5·250	14	442	1·479	1	815	1·138	6
201	4·890	4	620	1·453	1	822	1·131	2
204	3·103	100	606	1·444	1	727	1·105	2
220	3·023	81	622	1·427	1	4,4,10	1·077	5
400	2·619	7	428	1·379	4	10,0,2	1·038	2
224	2·376	3	624	1·359	10	729	1·024	1
322	2·225	4	540	1·342	1	4,0,14	1·012	2
404	2·167	28	527	1·333	2	10,0,4	1·009	2
420	1·981	3	800	1·310	2	660	1·006	2
008	1·922	9	608 802	1·293	6	842 828	0·983	4
208	1·804	6						
424	1·761	28	1,1,12	1·252	2	0,0,16	0·962	3
600	1·746	14	2,0,12	1·246	5	844	0·959	4
109	1·688	1	804	1·240	4	6,4,10	0·947	2
119	1·643	2	641	1·199	1	934	0·939	1
228	1·623	20	448	1·189	3	5,2,14	0·919	1
408	1·549	4	901	1·160	2	8,2,10 2,2,16	0·917	4
507	1·517	8	4,0,12	1·152	4			
			644	1·148	8	8,0,12	0·915	6

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* Communication from the Staff of the Research Laboratories of The General Electric Company Limited, Wembley, England.