8

CONTRIBUTION
No. 50

PHILIPS LABORATORIES, INC.
IRVINGTON - ON - HUDSON, N. Y.

EXTINCTION IN X-RAY DIFFRACTION PATTERNS OF POWDERS

By

A. R. LANG

Reprinted from the PROCEEDINGS OF THE PHYSICAL SOCIETY, Vol. 66, pp. 1003–1008, December, 1953

REPRINTED FROM THE
PROCEEDINGS OF THE PHYSICAL SOCIETY, B, VOL. LXVI, p. 1003, 1953

Extinction in X-Ray Diffraction Patterns of Powders

BY A. R. LANG
Philips Laboratories, Inc., Irvington-on-Hudson, N.Y., U.S.A.

MS. received 25*th August* 1952, *and in amended form* 24*th August* 1953

Abstract. Errors are pointed out in analyses by Hall and Williamson and by Weiss of extinction in powders. Formulae are proposed giving a first-order correction for the reduction of reflecting power of small spherical crystals due to primary and secondary extinction. Neither formula accounts adequately for differences between observed and calculated intensities in Hall and Williamson's measurements on copper and aluminium.

§ 1. INTRODUCTION

IT is nowadays possible to make precise measurements of the x-ray diffracting power of powders quite readily with the counter spectrometer. The observed diffracted intensity may, however, be influenced considerably by factors dependent upon the texture of the powder specimen. One such factor is extinction, and recent papers (Hall and Williamson 1951, Weiss 1952) have attempted to examine quantitatively its effect on the powder diffraction patterns of certain metals. In such studies it is necessary to consider how far the classical Darwin formulae are valid for the small particles which make up the powder specimen. It is also essential to ensure that these formulae are applied correctly. Hall and Williamson make errors in their analysis which largely invalidate the conclusions they draw. Weiss, too, makes errors, requiring his conclusions to be modified.

In both cases the errors principally concern the variation with diffraction angle of extinction losses. An attempt will here be made to state the correct formulae for this variation, applicable to the case when crystal-monochromatized radiation is used.

§ 2. PRIMARY EXTINCTION

Consider first primary extinction. If the value of the integrated reflection, in the absence of extinction, is denoted by ρ and the experimentally observed value by ρ', the well known Darwin correction for primary extinction is $\rho'/\rho = (\tanh mq)/mq$, where m is the number of planes occurring in regular succession and q is the amplitude reflected by a single plane, of spacing d,

$$q = \left(\frac{e^2}{mc^2}\right) N F d \lambda \times \text{polarization factor},$$

F is the structure amplitude of the plane and N is the number of unit cells per unit volume. It is convenient to denote the polarization factor by K where K is

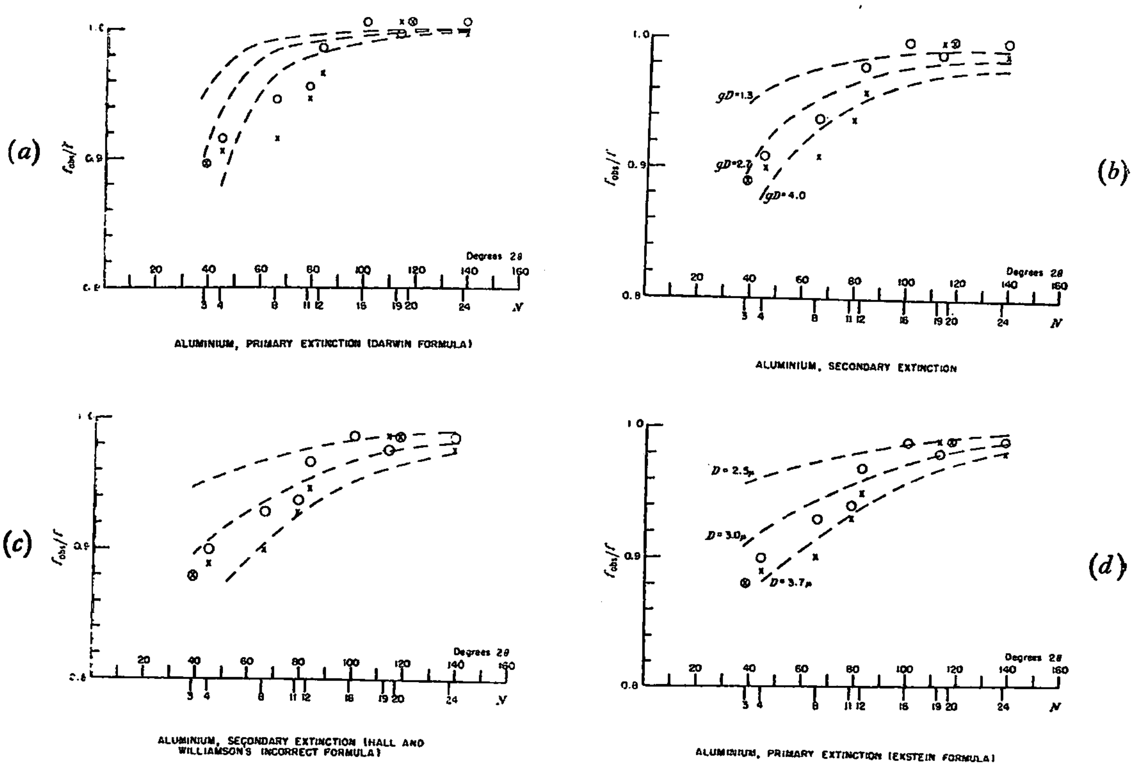

Fig. 1. Hall and Williamson's experimental f values for aluminium with extinction correction curves. (*a*) Darwin primary; (*b*) Darwin secondary; (*c*) Hall and Williamson's incorrect secondary; (*d*) Ekstein primary.

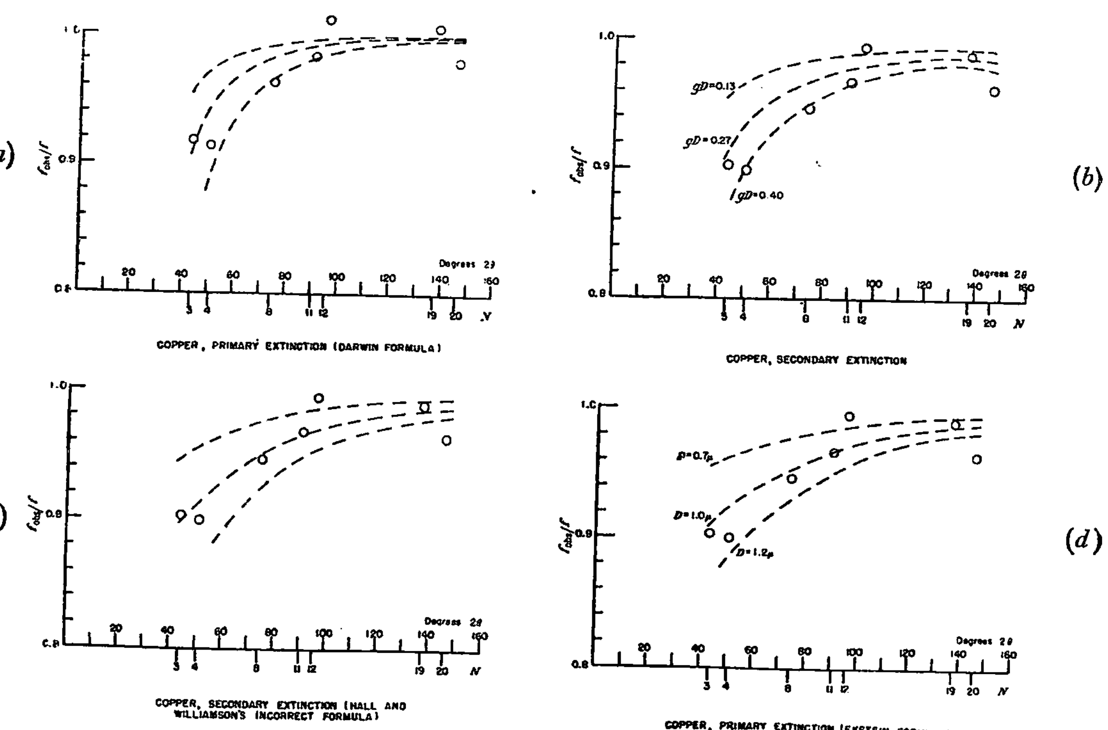

Fig. 2. Hall and Williamson's experimental f values for copper with extinction correction curves. (*a*) Darwin primary; (*b*) Darwin secondary; (*c*) Hall and Williamson's incorrect secondary; (*d*) Ekstein primary.

(*b*) Darwin secondary

$$\frac{f_{obs}}{f} = 1 - Bf^2\left(\frac{1}{\sin 2\theta}\right)\left(\frac{1+\cos^2 2\alpha\cos^4 2\theta}{1+\cos^2 2\alpha\cos^2 2\theta}\right).$$

(*c*) Hall and Williamson's incorrect secondary

$$f_{obs}/f = 1 - Cf^2.$$

(*d*) Ekstein primary

$$\frac{f_{obs}}{f} = 1 - Df^2\left(\frac{1+\cos^2 2\alpha\cos^4 2\theta}{1+\cos^2 2\alpha\cos^2 2\theta}\right).$$

In figs. 1 and 2, Hall and Williamson's experimental values of f_{obs}/f for both aluminium and copper, suitably scaled, have been fitted to these curves. In fig. 1 crosses represent Hall and Williamson's results quoted on p. 942 and circles those on p. 949.

The curves would undergo no significant modification if the monochromator were perfect. In the case of the quartz $10\bar{1}1$ reflection and CuKα radiation, as used by Hall and Williamson, $2\alpha = 26{\cdot}7°$, and substitution of $|\cos 2\alpha|$ in place of $\cos^2 2\alpha$ can cause a reduction of not more than $1\frac{1}{2}\%$ in the polarization factor in the correction term. This occurs at $2\theta \simeq 54°$ and 126°. The greatest possible reduction in the polarization factor occurs with $2\alpha = 64°$ and $2\theta = 49°$ or 131°, and then amounts to 5%. However, the value of f_{obs} derived from the observed integrated reflection depends upon the perfection of the monochromator through the factor $(1+\cos^2 2\alpha\cos^2 2\theta)/(1+\cos^2 2\alpha)$. Under Hall and Williamson's experimental conditions substitution of $|\cos 2\alpha|$ in place of $\cos^2 2\alpha$ in this expression increases f_{obs} at the most by $2{\cdot}6\%$, the greatest increase being in the region $2\theta = 90°$; as the fit of f_{obs}/f with all the extinction-correction curves is thereby worsened it may reasonably be concluded that their monochromator was effectively imperfect.

Though the difference between the Darwin secondary and Ekstein primary corrections is not large within the angular range under observation, it is greater than that suggested by Weiss. The scatter of the observations is considerable and there is no clear indication which fit is best, that for Ekstein primary being perhaps better than that for Darwin secondary. The values of D in both cases are reasonable; it is to be noted with what small crystallite sizes primary extinction may become appreciable. Hall and Williamson state that the particle sizes were $50\,\mu$ for aluminium and $2\,\mu$ for copper. The values of g derived on this basis are possible for aluminium but unlikely for copper. On balance, the evidence favours primary extinction in both cases, thus reversing the conclusions of Hall and Williamson.

Acknowledgment

The writer wishes to thank Dr. P. B. Hirsch of the Cavendish Laboratory, Cambridge, for advice on certain points.

References

Brindley, G. W., 1936, *Phil. Mag.*, **21,** 778.
Ekstein, H., 1951, *Phys. Rev.*, **83,** 721.
Evans, H. T., Jr., and Ekstein, M. G., 1952, *Acta Crystallogr., Camb.*, **5,** 540.
Hall, W. H., and Williamson, G. K., 1951, *Proc. Phys. Soc.* B, **64,** 937.
Taylor, A., 1944, *Phil. Mag.*, **35,** 215.
Weiss, R. J., 1952, *Proc. Phys. Soc.* B, **65,** 553.
Zachariasen, W. H., 1945, *Theory of X-Ray Diffraction in Crystals* (New York : Wiley).