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Comment on *A universal treatment of X-ray and neutron diffraction in crystals. I. Theory* by Hu (1997)

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Abstract

The re-interpretation by Hu [*Acta Cryst.* (1997), A**53**, 484–492] of the data of Mathieson [*Acta Cryst.* (1975), A**31**, 769–774] is shown to be fallacious by reference to the subsequent experimental measurements on the same LiF boule by Mathieson [*Acta Cryst.* (1977), A**33**, 610–617]. It is pointed out that a match of theoretical values with a set of experimental values does not, of itself, establish the physical reality of the assumptions underlying the theoretical model.

In the mid 1970's, I carried out measurements of the intensity of Bragg reflections from the surface of an LiF crystal over a wide range of asymmetry. There were two sets of measurements, both with the same LiF boule, one set with the surface abraded (Mathieson, 1975) (= M1) and, subsequently, the other with the surface polished flat to within one optical fringe (Mathieson, 1977) (= M2). The two sets were dramatically different. For the first, the plot of normalized intensity *versus* asymmetry was concave downwards (see Fig. 6 in M1), *i.e.* the normalized intensity decreased progressively with increase in asymmetry. This trend was interpreted in terms of the absorptive surface layer. For the second, the corresponding plot was concave upwards (see Fig. 4 in M2), *i.e.* the normalized intensity increased progressively with increase in asymmetry. This trend was interpreted as due to the progressive reduction of the effect of extinction on intensity.

Recently, Hu (1997) has used the experimental data in M1 and, ignoring the existence of the surface layer, has analysed the LiF situation as a single-component system. Within this context, she has succeeded, with appropriate selection of parameters, in curve-fitting my data (see her Fig. 8) virtually as well as I did on the basis of the surface layer (see Fig. 5 in M1). According to her theoretical analysis, the deviation of the experimental points from curve (*a*) (the kimematical limit curve) in her Fig. 8 is due to '*multiple reflections and not to a surface layer*'. Under her interpretation, the effect of multiple reflection, *i.e.* extinction, is to reduce the diffracted intensity and this effect *increases* with increasing asymmetry.

This interpretation by Hu is completely at odds with my experimental results in M2 where there was no abraded surface layer. Fig. 4 in M2 shows the increase in normalized intensity with increasing asymmetry, which results from the 'decoupling of multiple diffraction, leading to *reduction* of extinction' (see M2, p. 616). This latter conclusion is in accord with the earlier theoretical treatment of Hirsch & Ramachandran (1950) and with the normalized presentation of their curves that I gave in M2.

It is evident that if one forces a model to fit a preconceived notion (in this case that there is no surface layer), then theory may provide parameters so that calculated values closely fit experimental values but the physical situation implied by the parameters is not compatible with reality.

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Response to Mathieson's (1998) comment on *A universal treatment of X-ray and neutron diffraction in crystals. I. Theory*

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Abstract

There is an obvious difference between the behaviour of the dependence of the integrated reflection power ratio on the asymmetric parameter for plane crystals predicted by the H–D equations on mosaic crystals and that predicted by the theory of Hirsch & Ramachandran on perfect crystals. It is most important to get rid of the surface layer effect of the crystal sample as much as possible for the verification of such a difference by experiment. This paper is in response to the comment by Mathieson [*Acta Cryst.* (1998), A**54**, 251].

I did not include Mathieson's second experiment (Mathieson, 1977) (= M2) in my work (Hu, 1997) because he did not mention in any of his published articles that the sample with different cutting angle used in M2 was taken from the same

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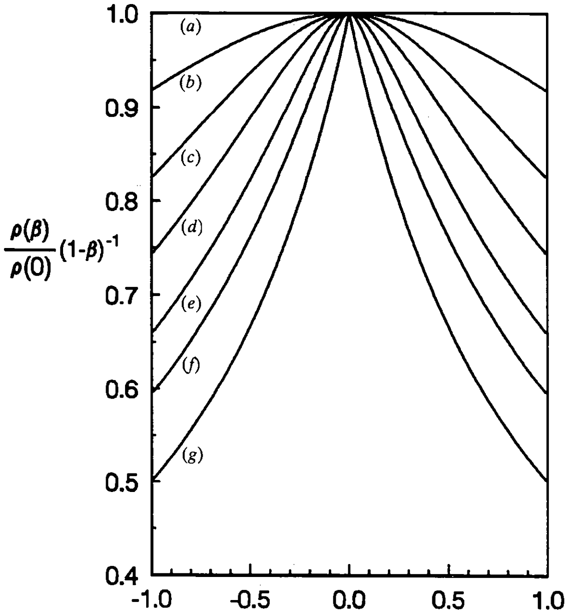

Fig. 1. The relationship between β and normalized integrated reflection power ratio for a plane mosaic crystal of infinite thickness in the Bragg case. Lines (*a*), (*b*), (*c*), (*d*), (*e*), (*f*) and (*g*) are for values of ξ_0 = 20.0, 0.5, 0.15, 0.05, 0.01, 0.001 and 0.0.

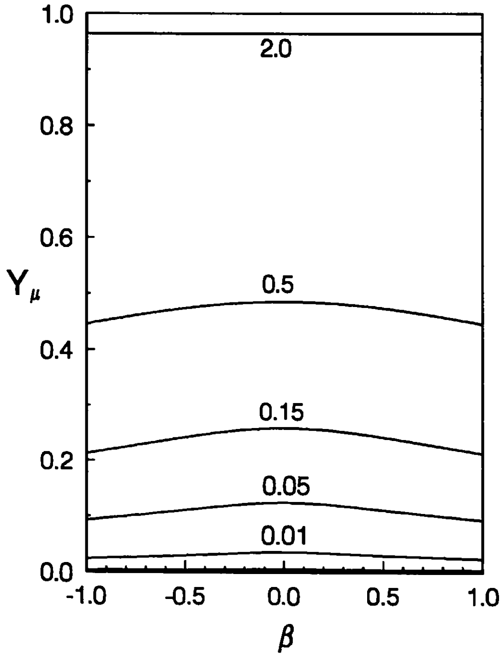

Fig. 2. The relationship between β and the secondary-extinction factor Y_μ for a plane mosaic crystal of infinite thickness in the Bragg case. The parameters on the curves are ξ_0. $Y_\mu(0) = 0.005$, when $\xi_0 = 0.001$. $Y_\mu(\beta) = 0$ when $\xi_0 = 0$. The values of $Y_\mu(\beta)$ hold up to $|\beta| = 0.99$.

boule used in Mathieson's first experiment (Mathieson, 1975) (= M1). However, I do not think this will pose a problem to my work. First, it is well known that even the crystals from the same boule can differ slightly in mosaicity. In Mathieson's experiment where the mosaic spread was rather narrow and the sample size was large, a slight difference in perfectness between the samples might cause a noticeable difference in their diffraction behaviour. Second, it is now clear that the property of the sample surface can have a very large influence on the shape of the measured normalized integrated reflection power ratio $\rho(\beta)(1-\beta)^{-1}/\rho(0)$ *vs* β (asymmetry) curve (*i.e.* NIRPRB curve).† Calculations based on the layer-coupling model for mosaic crystals (Hu, 1992) show that, by a proper adjustment of the parameters of a thin layer on the sample surface (*i.e.* η_{sur} and its thickness), one can almost simulate any shape of the measured NIRPRB curve from concave to convex. This means that this measured curve is unreliable unless the influence of the surface can otherwise be proved to be negligible.

The essence of the problem here, however, does not lie in the experiment itself but in the different conclusion derived from different theoretical approachs. The earlier theory of Hirsch & Ramachandran (1950) on perfect crystals predicted a set of concave NIRPRB curves, while the exact solution from the H–D equations for mosaic crystals predicted convex NIRPRB curves, as shown in Fig. 1. Its corresponding Y_μ *vs* β curves also display a less pronounced convex shape as shown in Fig. 2.

So it goes that the most conclusive check is to measure NIRPRB curves under more than two wavelengths on the *same* mosaic crystal sample with known dislocation density. The rocking curve should also be measured simultaneously and, if necessary, the sample surface should be treated under different conditions so that the effect of the surface layer, if any, can experimentally be proved negligible.

† Here ρ is identical with the symbol R_H^θ in Hu (1997).

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