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A note on the line profiles associated with mistakes.

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Introduction

There is an outstanding discrepancy between theory and experiment in connexion with the broadening of Debye–Scherrer lines or the diffuseness of 'single-crystal' reflexions from crystals with mistakes. The line profile in the former case, and the distribution of intensity in reciprocal space in the latter, are effectively the Fourier transforms of a function $J(t)$ or $J(x, y, z)$, where J is the mean value of the product FF^* of the structure factors of cells separated by a translation t perpendicular to the reflecting planes (for Debye–Scherrer lines) or x, y, z within the crystal ('single-crystal' reflexions) (Wilson, 1949, chap. 7). Simple theory, based on the assumption of mistakes at random, leads to an expression of the form

$$J(t) = J_0 \exp(-\gamma|t|), \quad (1)$$

where γ may depend on the indices of reflexion h, k, l; there is a similar three-dimensional analogue for $J(x,y,z)$. This 'Laplacian' form of $J(t)$ has a characteristic cusp at the origin, and falls off to zero rather rapidly with increasing t. On the other hand, experimentally derived values of $J(t)$ or $J(x, y, z)$ are more closely represented by a 'Gaussian' expression

$$J(t) = J_0 \exp(-\alpha t^2), \quad (2)$$

which is smoothly rounded at the origin and falls to zero much more rapidly with increasing t.

The 'experimental' values of J are in fact the result of a rather complex Fourier analysis, in which the recorded intensities of the broadened reflexions are 'unfolded' with similar unbroadened reflexions (Stokes, 1948). Rounding of J near the origin would result from the accumulation of experimental errors (photometry, slit width, etc.), the use of a finite instead of an infinite range of integration in the Fourier analysis (Eastabrook & Wilson, 1952), and perhaps from estimating the background at too high a level. MacGillavry & Strijk (1946) were content to attribute the non-Laplacian form of their curves to such difficulties, but this attribution becomes less plausible after the careful work of Edmunds & Hinde (1952) on $AuCu_3$, and more particularly the work of Steeple & Edmunds (1956) on $CdMg_3$. The latter made a special estimate of the possible distortion of a curve of the Laplacian type (equation (1)) through experimental difficulties and limited range of integration (they do not specifically mention background estimation), and concluded that the Gaussian shape was real, and not due to distortion of a Laplacian.

It is therefore of interest to see whether a model in which the mistakes do not occur at random would lead to essentially different results. In order to avoid complications, a layer structure will be considered, with mistakes in one direction only. As is well known, mistakes at random lead to a distribution of domain sizes of the type

$$p(\varepsilon) = \lambda \exp(-\lambda\varepsilon), \quad (3)$$

where $p(\varepsilon)d\varepsilon$ is the probability of the domain size lying within the range ε to $(\varepsilon+d\varepsilon)$, and λ is a parameter, easily seen to be equal to the reciprocal of the mean domain size. This distribution of domain sizes looks very like the Laplacian expression for $J(t)$, and one might jump to the conclusion that a Gaussian distribution of domain sizes would lead to a Gaussian expression for $J(t)$. Unfortunately the calculation of $J(t)$ from $p(\varepsilon)$ is not so simple, and has been done explicitly for only one other model, which may briefly be described as a 'nucleation' model instead of a 'growth' model. It will be shown below that *any* distribution of domains must produce an origin cusp in $J(t)$, but first the nucleation model will be discussed briefly.

Nucleation model

There are two remarkable early papers by Landau (1937) and Lifschitz (1937). Landau developed a growth model of mistakes in a simple form, and Lifschitz gave a general nucleation theory, including the growth model as a special case. Both papers have suffered an undeserved neglect, particularly as they are written in English. The writer first became acquainted with them about 1944.

The model of mistakes at random is tacitly based on crystallization (or structure transformation) starting at one place and proceeding with occasional mistakes. If structure transformation begins in many places (nucleation) and the nuclei grow until they meet, the junctions between domains no longer occur at random, but part way (halfway if all nuclei grow at the same rate) between the random positions of the nuclei. The size distribution of these elementary domains is easily found to be

$$p(\varepsilon) = \lambda^2\varepsilon \exp(-\lambda\varepsilon), \quad (4)$$

where λ is still the reciprocal of the mean elementary domain size. In general, however, there are only a few different kinds of unit cell possible, and there is a high probability (ranging from 1 in 2 for two kinds of cell down to about 1 in 6) that adjacent elementary domains will be physically indistinguishable, and hence to be counted as one larger domain. The effect of this is to shift the *form* of the distribution part way back from (4) towards (3), with an increase in the average domain size. Lifschitz obtained the general form of the domain-size distribution function; it reduces to (3) if the nuclei are very numerous and to (4) if the types of cell are very numerous. He also determined line profiles for layer structures of various types without explicitly evaluating $J(t)$.

Initial slope of $J(t)$

Let us consider the contribution of a typical domain Q to $J(t)$, measuring t in units of the interplanar spacing. For $t = 0$, F for each layer is multiplied by F^* for the *same* layer, and on the average each layer contributes

$$J_s \equiv \langle FF^* \rangle \quad (5)$$

to $J(0)$. For $t = 1$, F for each layer is multiplied by F^* for the adjacent layer. If the layers belong to the same

domain the average contribution will be J_s, as before, but for the layer on the extreme right of each domain F and F^* belong to *adjacent* domains, and the average contribution will be

$$J_a \equiv \langle F'F^* \rangle , \quad (6)$$

where the prime indicates that F and F' are the values of the structure factors of adjacent domains. If the total number of layers is N and the number of domain boundaries is K,

$$J(1) = N^{-1}[(N-K)J_s+KJ_a] , \quad (7)$$

it being assumed that N and K are so large that end effects can be neglected. On rearranging and putting $K/N = \lambda$, this becomes

$$J(1) = J_s-\lambda(J_s-J_a) . \quad (8)$$

For $t = 2$ the average contribution of each layer to $J(t)$ will be J_s for the $N-2K$ layers (approximately; the approximation consists in neglecting single-layer domains) for which F and F^* belong to the same domain, and J_a for the $2K$ layers (approximately) for which they belong to adjacent domains. The value of $J(t)$ is thus

$$J(2) \sim N^{-1}[(N-2K)J_s+2KJ_a] = J_s-2\lambda(J_s-J_a) , \quad (9)$$

and, in general, for small t,

$$J(t) \sim J_s-t\lambda(J_s-J_a) . \quad (10)$$

Now J_s is positive, from its definition. J_a is ordinarily negative—in a simple case (Wilson, 1949, p. 49) it is equal to $-J_s$ —but it cannot be greater in absolute value than J_s. For small t, therefore, $J(t)$ must decrease linearly with $|t|$, and thus has a cusp at the origin, like the Laplacian form, whatever the distribution function $p(\varepsilon)$. A similar argument for a cusp at the origin of $J(t)$ was given by MacGillavry & Strijk. The observed rounded origin must therefore be attributed either to a defect in the model of ordered domains separated by boundaries, or to experimental errors. One of the latter not explicitly discussed by Steeple & Edmunds (1956) is the estimation of the background level.

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The scattering of 4 Å neutrons by a beryllium crystal.

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Analysis of the reflexions of X-rays from beryllium has shown that the crystal has the hexagonal close-packed lattice with $c = 3{\cdot}58$ Å and $a = 2{\cdot}29$ Å (Gordon, 1949). Measurements of the energies of Bragg-reflected neutrons from a single beryllium crystal, used as monochromator on a neutron spectrometer (Pattenden & Baston, 1957), have shown appreciable intensities of low-energy neutrons which would not be expected if the crystal has the above structure. There appear to be first-order reflexions from (0001) and $(11\bar{2}1)$ planes, members of a class of planes which should have a zero atomic structure factor. Quantitative agreement between three different crystals suggested that the phenomenon might be a general property of beryllium crystals.

In order to verify that the effect was genuine, the following decisive experiment was performed.

A beryllium crystal, $1\frac{1}{4}$ in. $\times 1\frac{1}{4}$ in. $\times \frac{1}{4}$ in., was placed in a beryllium-filtered cold neutron beam containing a negligible number of neutrons with wavelengths shorter than 3·95 Å (Egelstaff & Pease, 1954; Butterworth *et al.*, 1957). Any Bragg reflexion, if observed, could be due to only the (0001) planes. Neutrons scattered through an angle of 73° from the beam were counted, corresponding to wavelengths of 4·26 Å for (0001) and 2·13 Å for (0002) Bragg reflexions. The arrangement is shown in Fig. 1. The results of a rocking-curve measurement are plotted

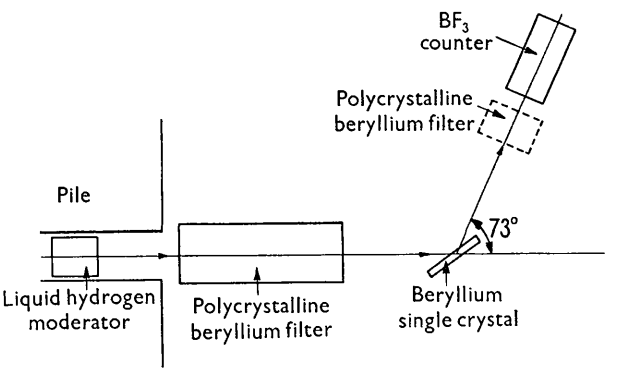

Fig. 1. Experimental arrangement.

in Fig. 2, and show an (elastically) scattered peak superimposed on a background of (inelastically) scattered neutrons. This interpretation was confirmed by placing a polycrystalline beryllium block in front of the detector.