the direction of the streaking caused by the thinness of the precipitates. Except for the few cases indicated in our table of observed and calculated structure factors (Auld & Coulsland, 1974), the reflections were sufficiently well separated to allow true integrated intensities to be measured for each reflection. For the above reasons, our recorded \( M' \) reflections were not chains of diffuse reflections and the comparison of observed intensities with those calculated by the usual structure factor method is appropriate.

(ii) As to the second objection, the chief disagreement between Régnier et al. and ourselves concerns the intensities of the 007, 113, 034 and 125 reflections of \( M' \). Régnier et al. did not observe any of these reflections whereas we observed all four; furthermore, the intensities of these four reflections, calculated for our proposed \( M' \) structure, were reasonably high. In the discussion that follows, the positions of \( M' \) and \( M \) reflections are given by coordinates referred to the \( <100>\) axes of the aluminium reciprocal lattice, taking \( d_{100\text{Al}}^* \) as one unit. The 007\(_{M'}\) reflection is found at positions of the type 1-17, 1-17, 1-17. As stated in our original Table 2, it was impossible to measure its intensity reliably, as it lies close to the 004\(_{Al}\) reflection at 1-09, 1-09, 1-09 and also to the very strong 111\(_{Al}\) reflection, Fig. 1. (Note that exposure times of about 100 h, used to record reflections from the \( M' \) phase, cause each aluminium reflection to be highly overexposed and so visible diffuse scattering extends a considerable distance from each node of the aluminium reciprocal lattice.) However, although the intensities of 007\(_{M'}\) and of 004\(_{Al}\) could not be reliably measured by the microdensitometer, both were definitely detectable by eye, with 007\(_{M'}\) fading and 004\(_{Al}\) strengthening as aging progressed. Similarly, the 113\(_{M'}\) reflections occur at positions of the type 1-17, 1-17, 0-83, also fairly close to 111\(_{Al}\) and to 112\(_{M}\) at 1-19, 1-19, 0-73, Fig. 1; these 113\(_{M'}\) reflections are nevertheless sufficiently well separated from the neighbouring reflections to permit approximate measurement. The 113\(_{M'}\) reflections also occur at positions of the type 0-17, 0-17, 1-83, in the vicinity of 200\(_{Al}\) and fairly close to 112\(_{M}\) at 0-09, 0-09, 1-83. While the intensities of the 007\(_{M'}\) and the 113\(_{M'}\) reflections were difficult to measure, these difficulties do not apply to the 034 and the 125 reflections of the \( M' \) phase, as these are well clear of any \( M \) or \( Al \) reflections. The 034\(_{M'}\) reflections are computed to lie at positions of the type 1-33, 2-67, 0-67 and were observed at this position on a zero-level \( \langle 112 \rangle^*_{Al} \) film. The 125\(_{M'}\) reflections are computed to occur at positions of the type 1-17, 1-50, 2-17 and 0-17, 0-50, 2-83. These positions are best found on upper-level photographs of \( \langle 112 \rangle^*_{Al} \), with \( \zeta = \frac{1}{3} d_{112Al}^* \) or of \( \langle 011 \rangle^*_{Al} \) with \( \zeta = \frac{1}{3} d_{110Al}^* \).

Again, these 125\(_{M'}\) reflections were present.

The intensity data for precipitates of this size and morphology are necessarily very poor compared with those required for precise crystal-structure determinations but, bearing this in mind, a fairly satisfactory fit to the data was found for the structure proposed. Hence we contend that the proposed \( M' \) structure is basically correct.

References


J. Rietveld analysis of powder neutron diffraction data displaying anisotropic crystallite size broadening. By

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Abstract

In order to accommodate anisotropic crystallite-size broadening effects in the Rietveld refinement of constant-wavelength powder neutron diffraction data, a modified function for the peak full width at half maximum has been evaluated for polycrystalline Ni(OH)\(_2\). The function resulted in significantly better agreement between observed and calculated profiles (the weighted residual \( R_w \) decreased from 14.1 to 8.5%), and structural standard deviations were reduced by an average of 43%.

Introduction

The value of powder neutron diffraction has increased dramatically in recent years owing largely to the development of structure refinement techniques based on the total profile rather than integrated intensities (Rietveld, 1967, 1969). Of fundamental importance to the success of these methods is the fact that, at constant wavelength, the peaks are simple Gaussian provided their full widths at half-maximum height (\( H \)) are determined by instrumental factors alone. Variation of \( H \) with \( 2\theta \) can be represented (Caglioti, Paoletti & Ricci, 1958) by

\[
H = \left[ U \tan^2\theta + V \tan \theta + W \right]^{1/2},
\]

where \( U, V, W \) are parameters refined during the analysis. However, for high-resolution diffractometers, complexities have been encountered owing to non-instrumental contributions to the peak profile, in particular from crystallite-size broadening. Such broadening results in a departure from a Gaussian shape, and more flexible peak-shape functions have therefore been proposed (Young & Wiles, 1982). With respect to changes in \( H \), although (1) has satisfactorily accommodated broadening effects for some samples (Santoro, D’Antonio & Caulder, 1983), a serious difficulty

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arises for crystallites with markedly anisotropic dimensions, such as for clay samples (Adams & Hewat, 1981), where crystallite broadening becomes a function of the scattering vector. This effect has been reported even for a ZnO sample (Langford, 1981). In the present study, the problem was encountered with Ni(OD)₂, crystals of which are plate-like with the trigonal axis (space group P₃₁₂₁) normal to the plates. This note indicates how a modified expression for $H$ has been successfully employed for structure refinement. Full details of the refined structure are to be submitted to Acta Crystallographica.

Experimental

Ni(OH)₂ was prepared by precipitation from NiSO₄ solution using KOH, and the very small crystal size was increased and D substitution effected by hydrothermal treatment using NaOD in D₂O. Infrared and mass spectroscopic estimates of the ratio D/(D+H) were 0.90(1) and 0.91(2). Neutron diffraction data were collected at 300 K on DIA at ILL using 1.386 Å neutrons and a 16 mm diameter vanadium container.

Results and discussion

With the assumption that peak broadening in Ni(OH)₂ is attributable to crystallite-size effects (Louer, Weigel & Langford, 1972), X-ray diffractometer full width at half maximum estimates implied average crystal platelet dimensions of 1800(200) Å diameter and 400(40) Å thickness. These values were found to be consistent with a transmission electron microscope examination of individual crystallites. Conventional profile analysis of powder neutron diffraction data, aimed mainly at determining the D location, involved refinement of eight structural parameters (allowing anisotropic motion for D alone) and eight additional parameters relating to peak shape, which was assumed Gaussian, and position. In all, the profile contained 41 resolvable reflections. The resultant weighted index, $R_w = 14.1\%$, was considerably higher than the statistical value of 2.5% expected for a correct model with an exactly correct peak-shape function.

Inspection of the observed and calculated profiles suggested that the principal cause of the high residual was anisotropic crystallite-size broadening. Fig. 1 demonstrates that whereas for 110 $H_{obs} < H_{calc}$, for 103 $H_{obs} > H_{calc}$, in accordance with increased broadening when the scattering vector is near the normal to the platelets, i.e. the [001] direction. The effect was not so apparent for the 001 reflections since these were all very weak. A function for $H$ was therefore introduced to allow variation with scattering vector. For a crystal platelet whose diameter is sufficiently large for broadening effects in this direction to be negligible, a correction can be developed in accordance with Fig. 2. Assuming the Scherrer relationship (Scherrer, 1918), the increase in $H$, $\Delta H$, for the general reflection $hkl$ is

$$\Delta H = K \lambda / t_{hkl} \cos \theta$$

$$= K \lambda \cos \varphi / t_{001} \cos \theta$$

$$= X \cos \varphi / \cos \theta.$$ 

If we assume

$$H = H_0 + \Delta H,$$  (2)

where $H_0$ corresponds to instrumental effects alone, then (1) may be extended to

$$H = [U \tan^2 \theta + V \tan \theta + W]^{1/2} + X \cos \varphi / \cos \theta.$$  (3)

Relationship (2) corresponds to the convolution of Cauchy peaks, whereas the instrumental neutron diffraction profile is Gaussian and that due to size effects is expected to be Cauchy (Jones, 1938; Alexander, 1948). However, since the convolution of a Gaussian with a Cauchy of variable $H$ results in an approximately linear relationship between $H_{total}$ and $H_{Cauchy}$ (Wertheim, Butler, West & Buchanan, 1974), the form of (3) was considered satisfactory for structure refinement although the indicated correlation between the constant, $X$, and $t_{001}$ will not now be exact.

For the sample in question, an additional complication arises since the platelet diameter is such that broadening cannot be ignored for $hk0$ reflections, and (3) may therefore appear unsatisfactory. However, it has been reported that (1) can accommodate isotropic broadening by adjustments to $U$ and $W$ (Santoro, D’Antonio & Caulder, 1983), and consequently the above relationship (3) was tested with the assumption that the correction constant, $X$, would compensate for the increased breadth of a general reflection relative to a hypothetical $hk0$ reflection at the same $\theta$.

On the basis of the crystallite dimensions determined from X-ray diffraction, $X$ was estimated to be $0.14(20)$, and when (3) was introduced into the refinement $R_w$ dropped to

![Fig. 1. Observed (•), calculated and difference profiles of 110 and 103 reflections using standard half-width function.](image)

![Fig. 2. Variation of crystal thickness with scattering vector.](image)
When \( X \) was allowed to vary the best agreement (\( R_w = 8.5\% \)) resulted for \( X = 0.18 \). Comparison of the \( U, V, W \) parameters with those relating to instrumental broadening alone results in a neutron diffraction crystallite-size estimate of 1850 Å diameter and 330 Å thickness, which agree satisfactorily with those from X-ray diffraction. The observed and calculated profiles for 110 and 103, Fig. 3, now imply no serious error in \( H \). The improved function for \( H \) resulted in no major changes to the structural parameters, but e.s.d.'s were all reduced, the average reduction being 43%. It is also relevant to note that, whereas the conventional treatment resulted in a refined \( D \) scattering length consistent with \( D/(D+H) = 0.97(2) \), the modified relationship provided the value 0.885(7), which is now in good agreement with infrared and mass spectroscopy evaluations.

The success of the simple treatment illustrated suggests possible application to other occurrences of \( hkl \)-dependent peak broadening, especially to systems showing pronounced uniaxial symmetry. The observation of such effects is expected to become more common as diffractometer resolution increases and pulsed sources become more widely available.

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References