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Structural Refinement of Neutron and X-Ray Data by the Rietveld Method: Application to Al_2O_3 and $BiVO_4$

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Abstract

The application of the Rietveld refinement technique to neutron and x-ray powder data from standard samples of Al_2O_3 is described. The results are compared with those obtained by conventional refinements of the corresponding integrated intensities, and also with x-ray single crystal data. The Rietveld technique has also been used to analyze neutron and x-ray powder data in a structural study of $BiVO_4$. Since V has a very small neutron scattering amplitude, the x-ray data allow a more accurate determination of the V position to be made.

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The use of the Rietveld technique for refinement of powder diffraction data has been reviewed in these proceedings by Hewat[1] and Young[2] for the case of neutrons and x-rays, respectively. The neutron technique is now firmly established and has been used in hundreds of structural investigations, but the x-ray technique is still in its infancy, and a number of fundamental problems remain. Chief among these are the lack of a suitable function to describe the peak shape, and where to truncate the peak tails. It may also be necessary to make allowance for preferred orientation.

The possibility of combining the powerful Rietveld technique with the better resolution of x-ray diffractometers provides a powerful stimulus for overcoming these limitations. In addition, the availability of monochromated radiation from synchrotron sources in the next few years offers the prospect of obtaining very high resolution powder data with peak profiles which are much closer to Gaussian.

One approach to the analysis of x-ray powder data is described in these proceedings by Parrish and Huang.[3] In this, integrated intensities can be obtained by deconvolution of powder data with the aid of measured values of the full profiles of a number of standard specimens. As far as is known, this technique has not yet been applied in structural refinement. A more common current approach, as described by Young,[2] is to modify the Rietveld program for neutron refinement. In the present work, this has been done as simply as possible. A comparison is made between the results obtained in refinements of neutron and x-ray data for Al_2O_3, which is a commonly used standard, and $BiVO_4$, which undergoes an interesting ferroelastic phase transition at 255°C.[4]

The neutron data from Al_2O_3 were collected for an intercomparison project of the Neutron Diffraction Commission of the International Union of Crystallography.[5] The sample was a sintered pellet made from Linde A grade Al_2O_3[6] about 1.4 cm in diameter and 1.8 cm in length weighing 10.5 g. Pyrolytic graphite was used as

monochromator in the (002) reflection setting to give neutrons of wavelength 1.424 Å, and as an analyzer in the (004) setting. Higher order components of wavelength were removed with a graphite filter. Collimation was 20' in-pile, 40' monochromator-to-sample, 40' sample-to-analyzer, and 10' analyzer-to-counter. Data were collected at 0.05° steps over a 2θ range of 22.0 - 124.4° with a counting time of 38 seconds per step. Refinement was carried out with a modified version[7] of the Rietveld program[8] with individual isotropic temperature factors. Scattering amplitudes were taken as 0.345 and 0.580×10^{-12} cm for Al and O, respectively. The results are summarized in Table 1, and the fitted profile is shown in Figure 1. Agreement is very good, as seen by comparison of R_{WP}, the weighted profile R factor, with R_E, the expected, or statistical, value (for definitions, see reference 7).

The x-ray data were collected on a General Electric XRD-5 diffractometer with a fine-focus Cu target (take-off angle 6°) and a bent graphite monochromator of normal mosaic spread 0.4° in the diffracted beam tuned for Cu Kβ radiation. The sample consisted of a pressed pellet of NBS 0.3 μm Al_2O_3 powder which had been sintered overnight at 1000°C. Collimation consisted of a standard 1° horizontal divergence collimator with medium resolution Soller slits in the incident beam, and medium resolution Soller slits and an 0.05° receiving slit in the diffracted beam. Data were collected at 0.02° steps over selected ranges of 2θ between 22° and 136° with counting times ranging between 20 and 80 seconds according to the intensity of the peak.

A scan of the (116) peak is shown in Figure 2a, and for comparison, the corresponding neutron scan in Figure 2b. A Gaussian peak gives a good fit to the latter as shown by the solid line, with $R_{WP} = 0.038$ ($R_E = 0.031$). The x-ray data in Figure 2a were fitted to three Lorentzian functions of the type $A/[1 + C(\Delta 2\theta)^2]^n$; a simple Lorentzian L(n = 1), an intermediate IL(n = 1.5), and a modified ML(n = 2). The results are summarized in Table 2, and it can be seen that the quality of the fit is not as good as in the neutron case. The intermediate function gives

the best fit over this range of data, which is about five full-widths at half-maximum (FWHM), and is shown as a solid line in Figure 2a.

A modified version of the Rietveld program described previously[10] was used to refine the x-ray data, which were fitted to the intermediate Lorentz function over a range of 2 FWHM's on each side. Scattering factors for Al^{3+} [11] and O^{2-} [12] corrected for the real dispersion term were used. At present the program has not been modified to incorporate the imaginary dispersion term. The initial fit was quite encouraging (R_{WP} = 0.165, R_E = 0.066), but the intensities showed unmistakable evidence of [001] preferred orientation. In Rietveld's original program,[8] provision is made for a correction of the type $I_{corr} = I_{obs}\exp(-G\phi^2)$ where ϕ is the acute angle between the scattering vector and the normal to the crystallites. G is the preferred orientation parameter and is a measure of the half-width of the assumed Gaussian distribution of the normals about the preferred orientation direction, which is along the axis of the cylindrical samples usually used in powder neutron diffraction. This expression is not appropriate for flat-plate x-ray samples, but inspection of the observed and calculated intensities showed an exponential-type dependence which could be approximated by a slightly modified expression of the type $I_{corr} = I_{obs}\exp[-G(\pi/2 - \phi)^2]$. With this correction, most of the systematic discrepancies disappeared and R_{WP} showed a significant decrease to 0.149. This is illustrated in Figure 3, which shows the ratio of the observed and calculated intensities for several of the stronger peaks with and without the correction.

The results of the refinement are summarized in Table 1, and the profile fit is shown in Figure 4, with all intensities normalized to a counting time of 40 seconds.

Integrated neutron and x-ray intensities were determined and refined with a program which allows overlapping peaks to be included. The final results are also summarized in Table 1, together with some recent x-ray single crystal results.[13]

There is agreement among the various sets of positional parameters to within 1-2 esd's. However the esd's derived from the integrated intensities are a factor of 2-3 higher than those from the profile refinements. This subject is discussed in more detail by Cooper et al.[14] elsewhere in the proceedings.

The x-ray profile temperature factors are clearly systematically high by a factor of two or so. Since the integrated values are in reasonable agreement with the neutron values, it is likely that the problem lies in the peak shape function rather than in other possible sources of error such as surface roughness, choice of scattering factors or the Lorentz-polarization correction.

The difference between the neutron and x-ray lattice parameters determined in the profile refinements can be largely accounted for by a small error in the neutron wavelength of about 0.13%. The apparent precision of the x-ray values is rather unexpected, since no attempt was made to allow for systematic deviations in peak positions as a function of 2θ or aberrations in peak shape. This precision could be quite valuable in investigations of phase transitions or thermal expansion behavior.

The observed and fitted values of peak FWHM's are shown as a function of 2θ in Figure 5 for the neutron and x-ray profile refinements. The usual expression $(\mathrm{FWHM})^2 = U \tan^2\theta + V \tan\theta + W$ has been employed in both cases.

The x-ray Rietveld technique has been used in conjunction with the neutron technique in a structural study of $BiVO_4$.[15] This has monoclinic symmetry at room temperature and undergoes a ferroelastic structural transition at 255°C to a tetragonal scheelite-type structure. The neutron scattering amplitude of V is small, about -0.05×10^{-12} cm, and the V shifts from the ideal scheelite positions are rather poorly determined ($\sim$0.06 Å, $\sigma = 0.03_5$Å) in the neutron refinement. An x-ray refinement was accordingly undertaken in order to obtain a more accurate value. A comparison of the neutron and x-ray results is given in Table 3, and

the fitted profiles are shown in Figures 6 and 7. Once again, in the initial stages of the x-ray refinement systematic discrepancies were observed which indicate [001] preferred orientation. Inclusion of a correction of the form described earlier gave a much-improved fit, with R_{WP} decreasing from 0.223 to 0.178.

From Table 3 it can be seen that the Bi positional parameters are equally well determined in the two refinements, while those of vanadium and oxygen are a factor of about five better determined in the x-ray and neutron refinements, respectively, as is to be expected from the relative scattering amplitudes. Agreement is generally within 2-3 esd's. Although these may be underestimated as discussed by Cooper et al.,[14] it seems likely that part of the disagreement lies in systematic errors in the x-ray analysis. This certainly appears to be the case for the temperature factors, where agreement is very poor. It is to be noted that the neutron results, including temperature factors, are in better agreement (1-2 esd's) with those of an independent neutron study by David et al.[16]

There is once again a small systematic difference between the neutron and x-ray lattice parameters which reflects an 0.05% error in the neutron wavelength. The two values of the monoclinic angle γ, which is independent of wavelength, are in excellent agreement. The precision of the x-ray values is again quite striking.

From the above comparisons, one can conclude that the refinement of x-ray data by the Rietveld technique can give useful results for the positional parameters in spite of the problems of peak shape, truncation, and aberrations. However, further work in this area is obviously necessary. One useful approach is suggested by the work of Wertheim et al.,[(17)] in which a Voight line shape is approximated by a linear combination of Gaussian and Lorentzian components. Such an approximation gives a significantly better fit to the data in Figure 2a, R_{WP} decreasing to 0.070. It is also necessary to obtain more rigorous expressions for the angular dependence of the FWHM, and for preferred orientation.

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References

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Table 1

Results of structure refinements for Al_2O_3. N(hkl) is the number of reflections used in the refinement. Other quantities are defined in text or ref. 7. R_I and R_{WP} are based on point-by-point or integrated intensities as appropriate. A value of 0.04 $Å^2$ has been added to the neutron B's to allow for the effects of absorption as described by Hewat.[9]

Parameter	Neutron (1.424 Å)		X-ray (1.392 Å)		x-ray Crystal[12]
	Profile	Integrated	Profile	Integrated	
Al:z	0.35221(8)	0.3521(2)	0.35200(7)	0.3522(2)	0.35219(1)
Al:B($Å^2$)	0.22(2)	0.26(5)	0.40(1)	0.24(6)	----
O:x	0.30636(9)	0.3060(2)	0.3064(3)	0.3066(8)	0.30633(5)
O:B($Å^2$)	0.23(1)	0.25(3)	0.51(2)	0.15(8)	----
G(rad^{-2})	----	----	0.195(9)	0.19(3)	----
a(Å)	4.7640(1)	----	4.75855(2)	----	----
c(Å)	13.0091(3)	----	12.9906(1)	----	----
U(deg^2)	1.42(11)	----	0.0084(12)	----	----
V(deg^2)	-1.62(14)	----	0.0117(19)	----	----
W(deg^2)	0.55(4)	----	0.0073(6)	----	----
R_I	0.018	0.019	0.038	0.053	----
R_{WP}	0.071	0.024	0.149	0.082	----
R_E	0.060	----	0.111	----	----
N(hkl)	60	60	69	71	----

Table 2

Results of least-squares fits to the data in Figure 2. Background was determined well away from the peak, and was not a variable in the refinement. NO is the number of observations.

	X-Ray (1.392 Å)			Neutron (1.424 Å)
	L	IL	ML	G
Peak amplitude	2224(76)	2054(53)	1958(70)	4359(40)
Peak position (deg)	51.494(2)	51.494(2)	51.493(2)	52.77(1)
FWHM (deg)	0.100(3)	0.121(3)	0.132(4)	0.312(2)
Background	←	21.3	→	35.3
R_{WP}	0.106	0.086	0.124	0.038
R_E	←	0.041	→	0.031
NO	←	31	→	32

Table 3

Structural parameters for $BiVO_4$ at 295K from Rietveld refinement of neutron and x-ray powder data. N(hkl) is the number of reflections used in the refinement.

	Neutron (1.302 Å)	X-ray (1.392 Å)
Bi:z	0.6335(2)	0.6341(2)
Bi:B(Å^2)	0.80(3)	0.36(2)
V:z	0.130(3)	0.1315(6)
V:B(Å^2)	-0.3(4)	0.13(6)
O(1):x	0.1465(4)	0.143(3)
O(1):y	0.5077(4)	0.512(3)
O(1):z	0.2082(2)	0.211(1)
O(1):B(Å^2)	0.85(4)	1.9(2)
O(2):x	0.2606(5)	0.252(3)
O(2):y	0.3810(4)	0.362(4)
O(2):z	0.4493(2)	0.446(1)
O(2):B(Å^2)	0.85(4)	2.0(2)
G(rad^{-2})	----	0.30(1)
a(Å)	5.1935(3)	5.1956(1)
b(Å)	5.0898(3)	5.0935(1)
c(Å)	11.6972(8)	11.7044(2)
γ(deg)	90.387(4)	90.383(1)
U(deg^2)	2.53(6)	0.049(7)
V(deg^2)	-2.03(6)	-0.020(6)
W(deg^2)	0.495(13)	0.0165(11)
R_I	0.028	0.077
R_{WP}	0.123	0.178
R_E	0.117	0.097
N(hkl)	391	154

Figure Captions

Figure 1. Neutron profile fit and difference pattern for Al_2O_3.

Figure 2. Diffraction data for the (116) reflection of Al_2O_3: (a) X-rays, Cu $K\beta$; (b) Neutrons. Solid lines are fitted curves as described in text.

Figure 3. Ratio of observed and calculated integrated x-ray intensities for Al_2O_3 as a function of ϕ, the angle between the normal to the plane hkl and the [001] axis. Open circles - no correction. Closed circles - preferred orientation correction applied.

Figure 4. X-ray profile fit and difference pattern for Al_2O_3.

Figure 5. Variation of FWHM of Al_2O_3 diffraction peaks as a function of scattering angle 2θ for the experimental conditions listed. (a) X-rays, Cu $K\beta$; (b) Neutrons, λ = 1.424 Å.

Figure 6. Neutron profile fit and difference pattern for $BiVO_4$ at 295K. Scattering amplitudes taken as 0.852, -0.052 and 0.580 x 10^{-12} cm for Bi V and O, respectively.

Figure 7. X-ray profile fit and difference pattern for $BiVO_4$ at 295K. Scattering factors for Bi^{3+} and V^{5+} taken from ref. 11, and for O^{2-} from ref. 12. Peaks have been fitted over a range of 2.5 FWHM's.

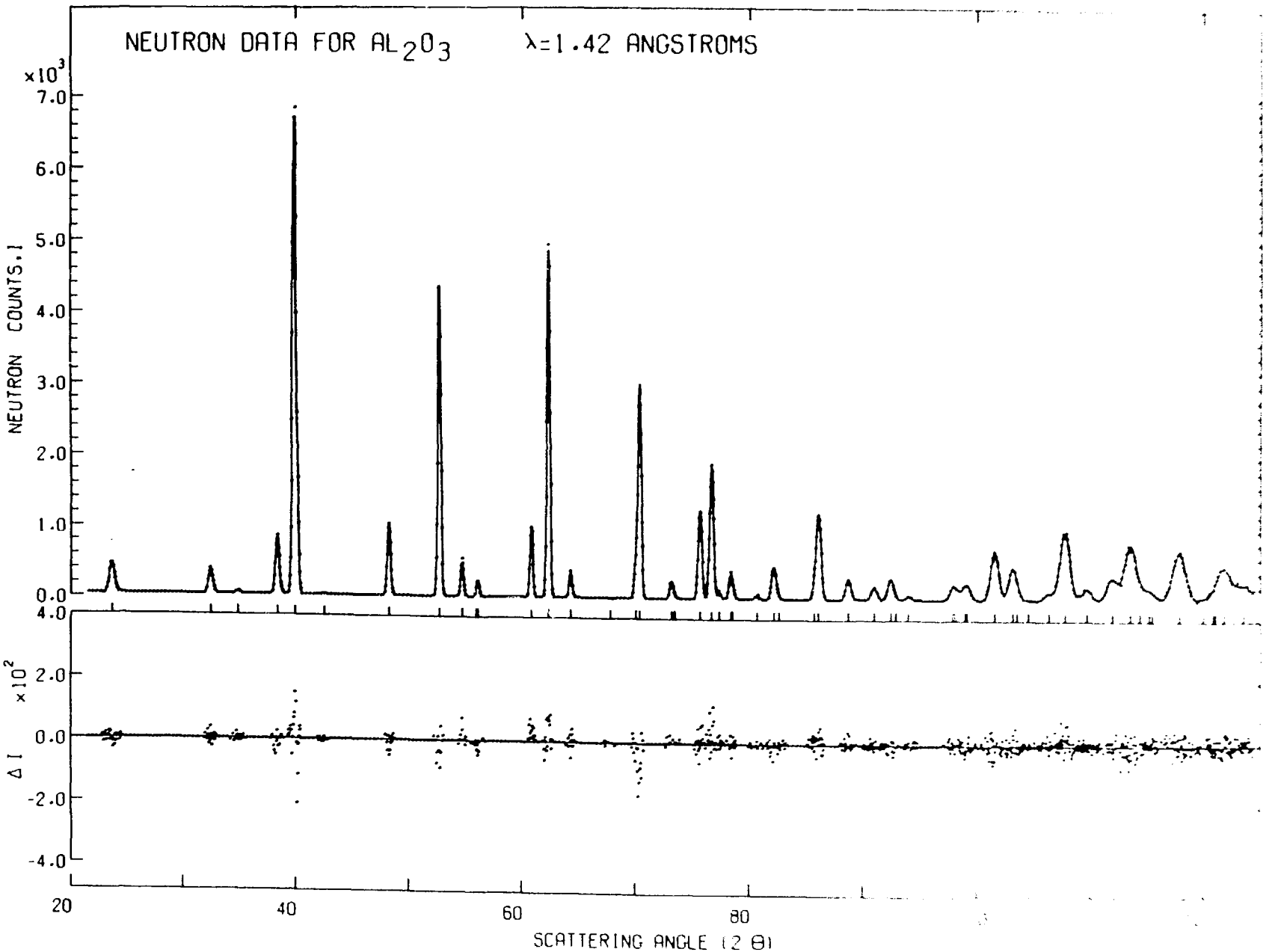
NEUTRON DATA FOR AL_2O_3
λ=1.42 ANGSTROMS
×10³
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
NEUTRON COUNTS, I
4.0
2.0
0.0
-2.0
-4.0
×10²
ΔI
20
40
60
80
SCATTERING ANGLE (2 θ)

FIGURE 1

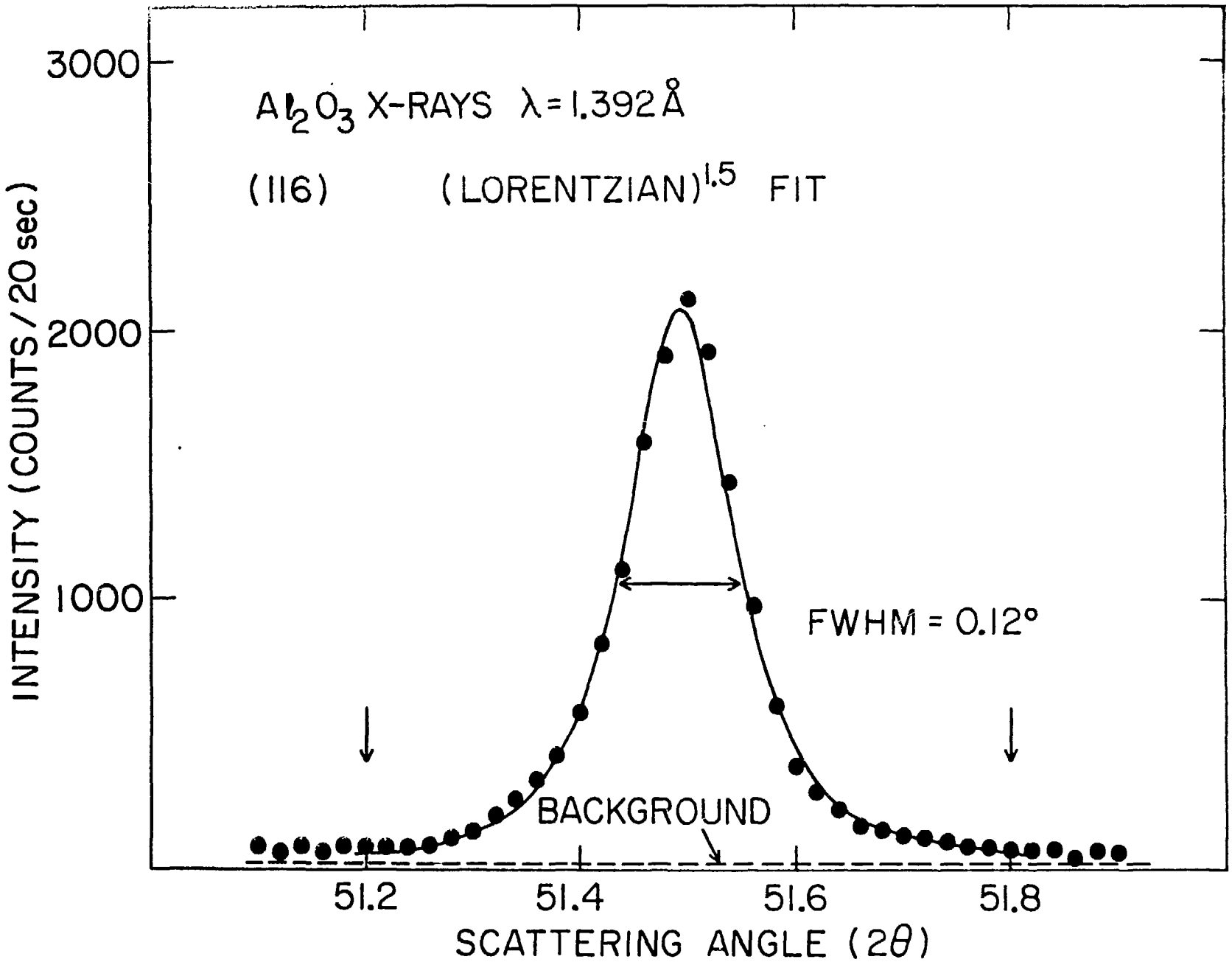
Al_2O_3 X-RAYS $\lambda = 1.392$ Å
(116) (LORENTZIAN)$^{1.5}$ FIT
FWHM = 0.12°
BACKGROUND
INTENSITY (COUNTS / 20 sec)
3000
2000
1000
51.2
51.4
51.6
51.8
SCATTERING ANGLE (2θ)

FIGURE 2a

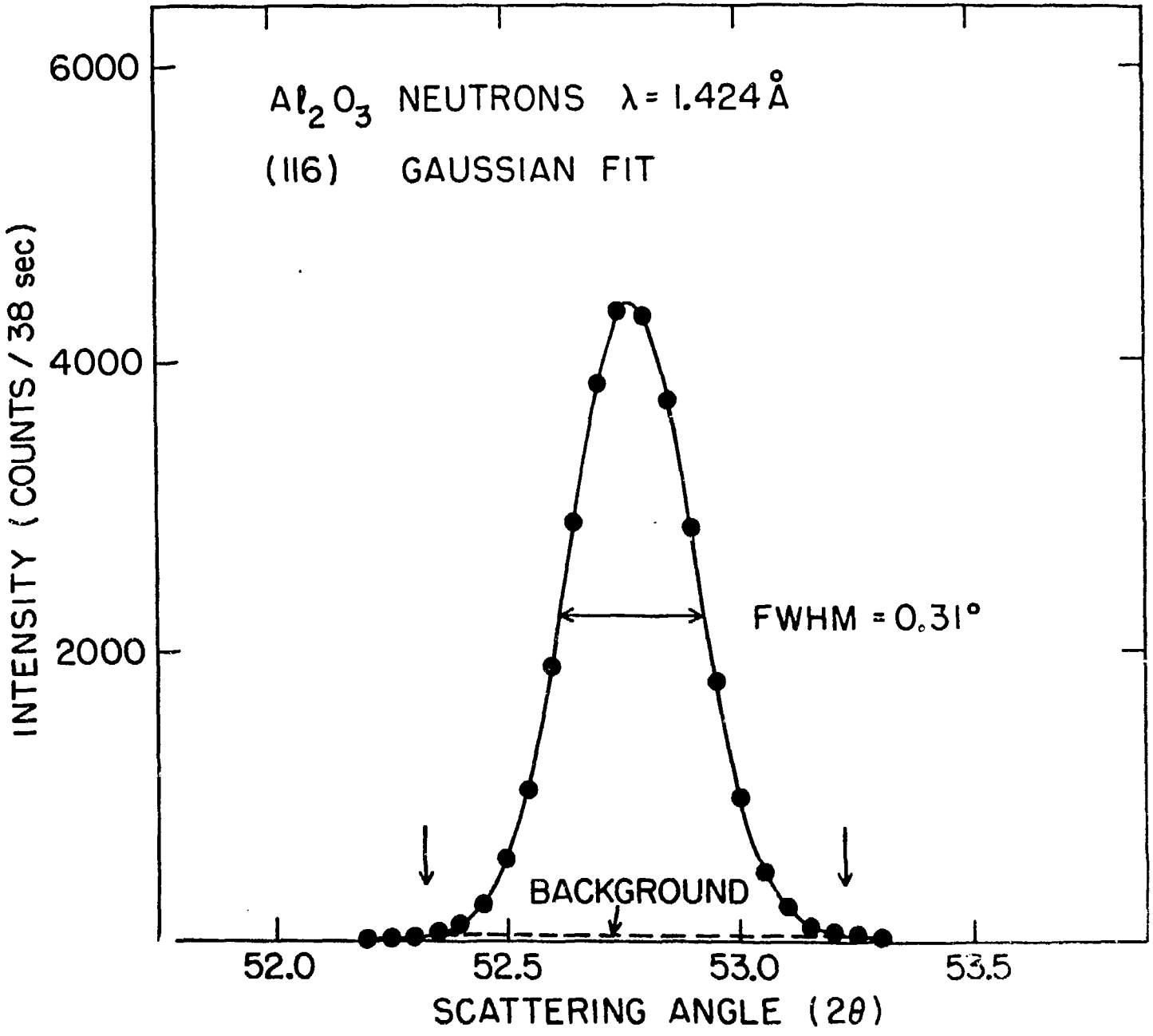
Al_2O_3 NEUTRONS $\lambda = 1.424$ Å
(116) GAUSSIAN FIT
FWHM = 0.31°
BACKGROUND
6000
4000
2000
INTENSITY (COUNTS / 38 sec)
52.0
52.5
53.0
53.5
SCATTERING ANGLE (2θ)

FIGURE 2b

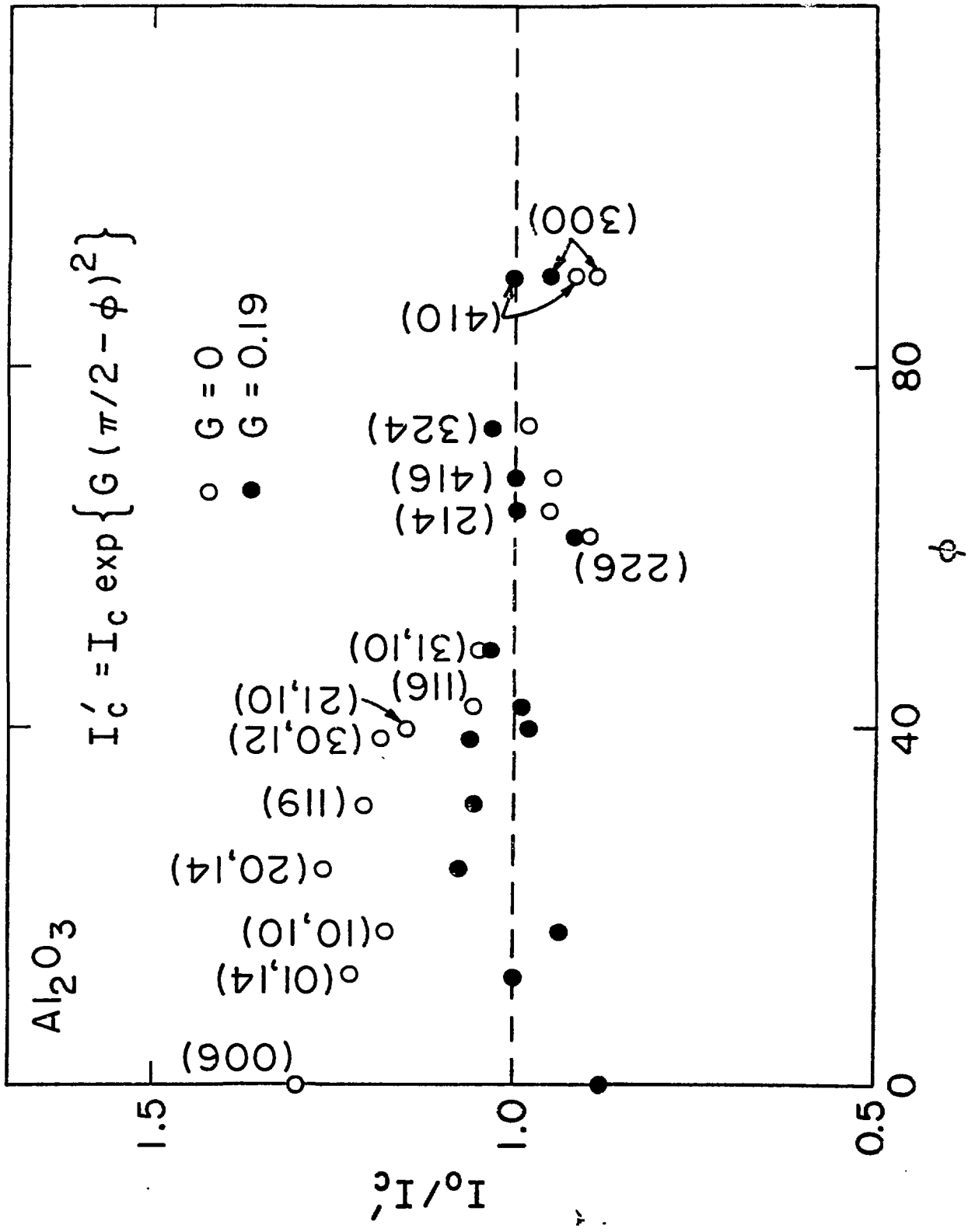
$I_c' = I_c \exp\left\{G(\pi/2-\phi)^2\right\}$
G = 0
G = 0.19
Al_2O_3
(006)
(01,14)
(10,10)
(20,14)
(119)
(30,12)
(21,10)
(116)
(31,10)
(226)
(214)
(416)
(324)
(410)
(300)
I_o/I_c'
1.5
1.0
0.5
0
40
80
ϕ

FIGURE 3

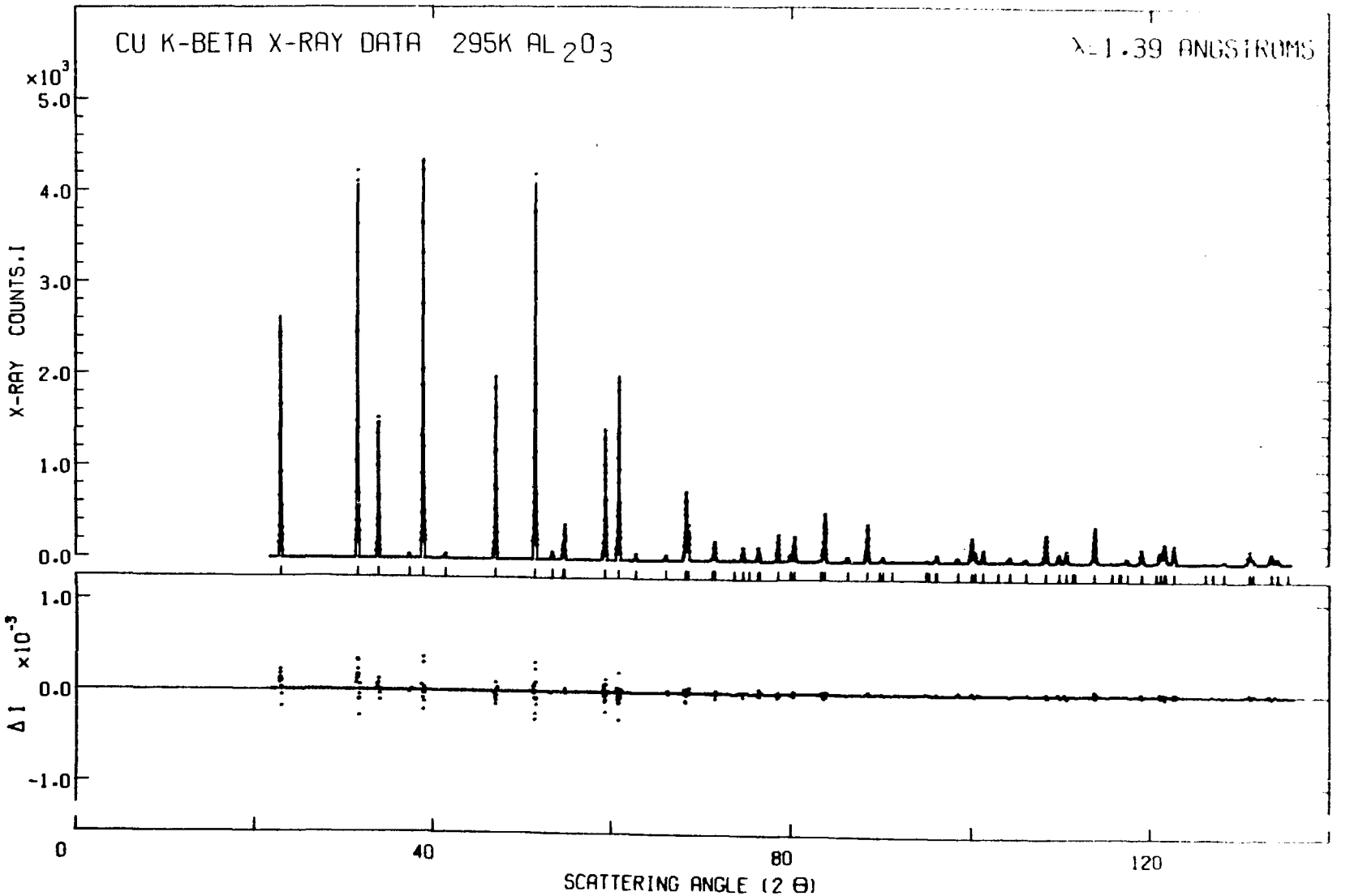
CU K-BETA X-RAY DATA 295K AL2O3
λ=1.39 ANGSTROMS
X-RAY COUNTS,I
×10³
5.0
4.0
3.0
2.0
1.0
0.0
ΔI ×10⁻³
1.0
0.0
-1.0
0
40
80
120
SCATTERING ANGLE (2 θ)

Figure 4

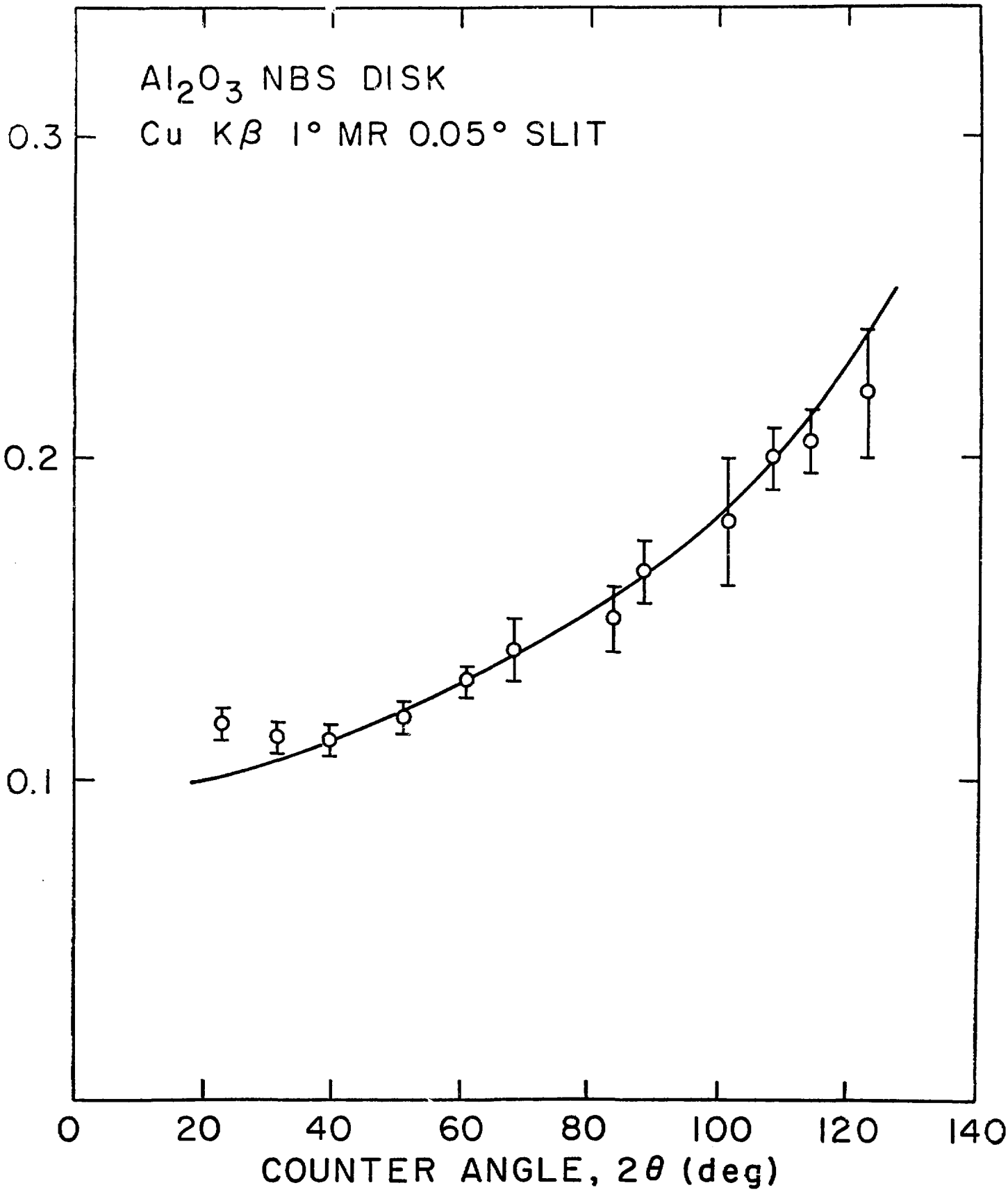
Al_2O_3 NBS DISK
Cu Kβ 1° MR 0.05° SLIT
0.3
0.2
0.1
0
20
40
60
80
100
120
140
COUNTER ANGLE, 2θ (deg)

FIGURE 5a

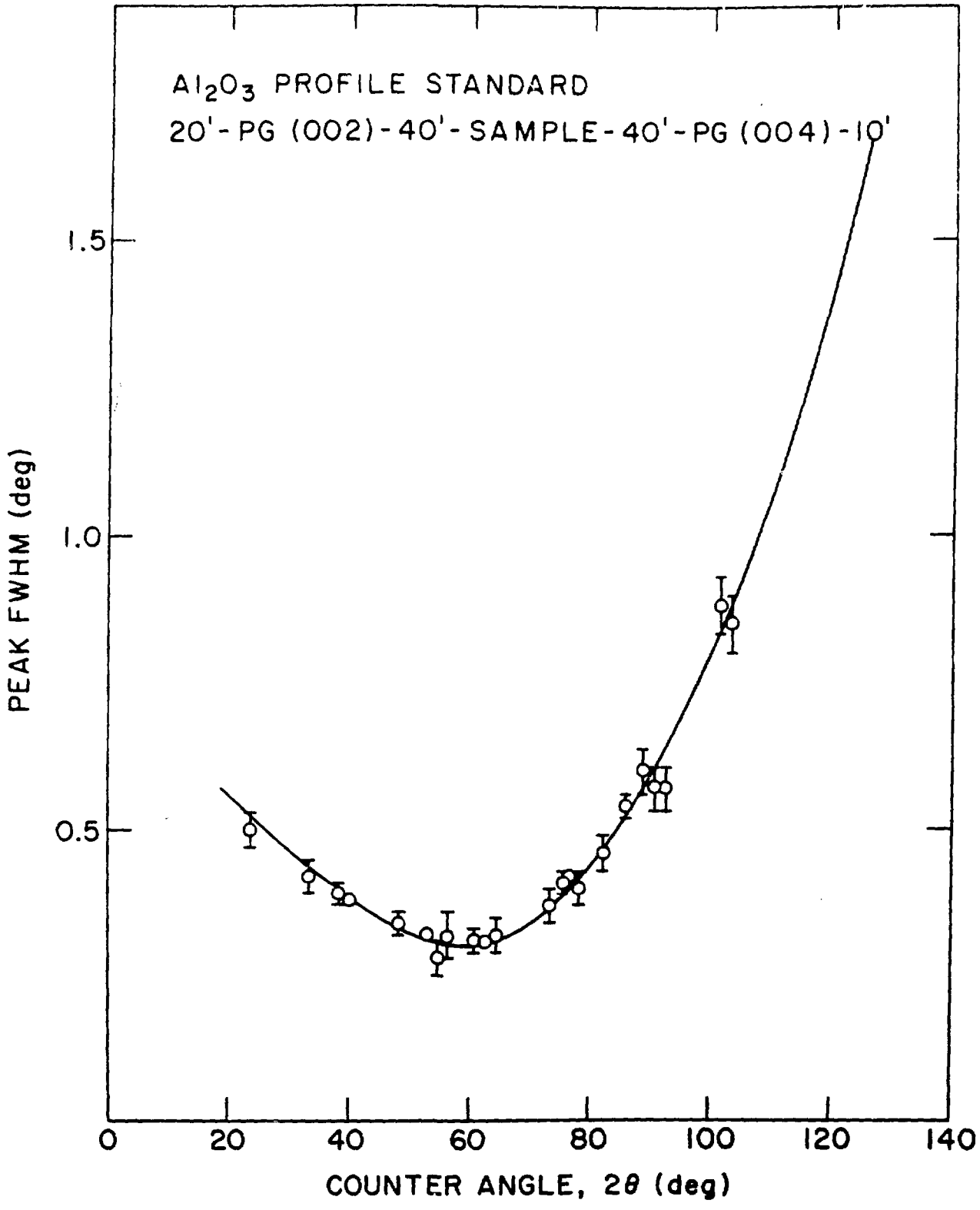
Al_2O_3 PROFILE STANDARD
20'-PG (002)-40'-SAMPLE-40'-PG (004)-10'
PEAK FWHM (deg)
1.5
1.0
0.5
0
20
40
60
80
100
120
140
COUNTER ANGLE, 2θ (deg)

FIGURE 5b

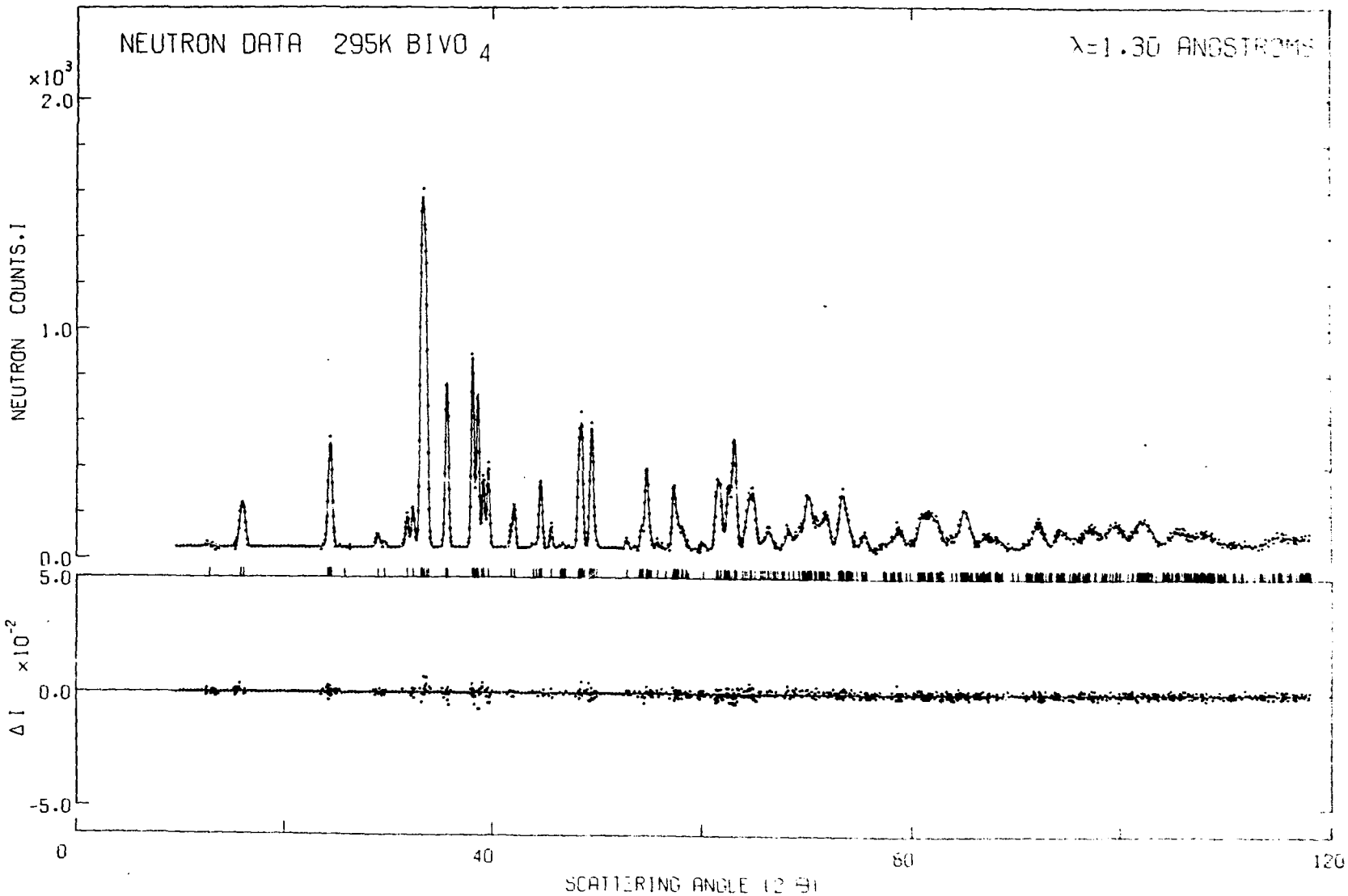
NEUTRON DATA 295K BIVO 4
λ=1.30 ANGSTROMS
×10³
2.0
1.0
0.0
NEUTRON COUNTS.I
5.0
0.0
-5.0
Δ I ×10⁻²
0
40
80
120
SCATTERING ANGLE (2 θ)

FIGURE 6

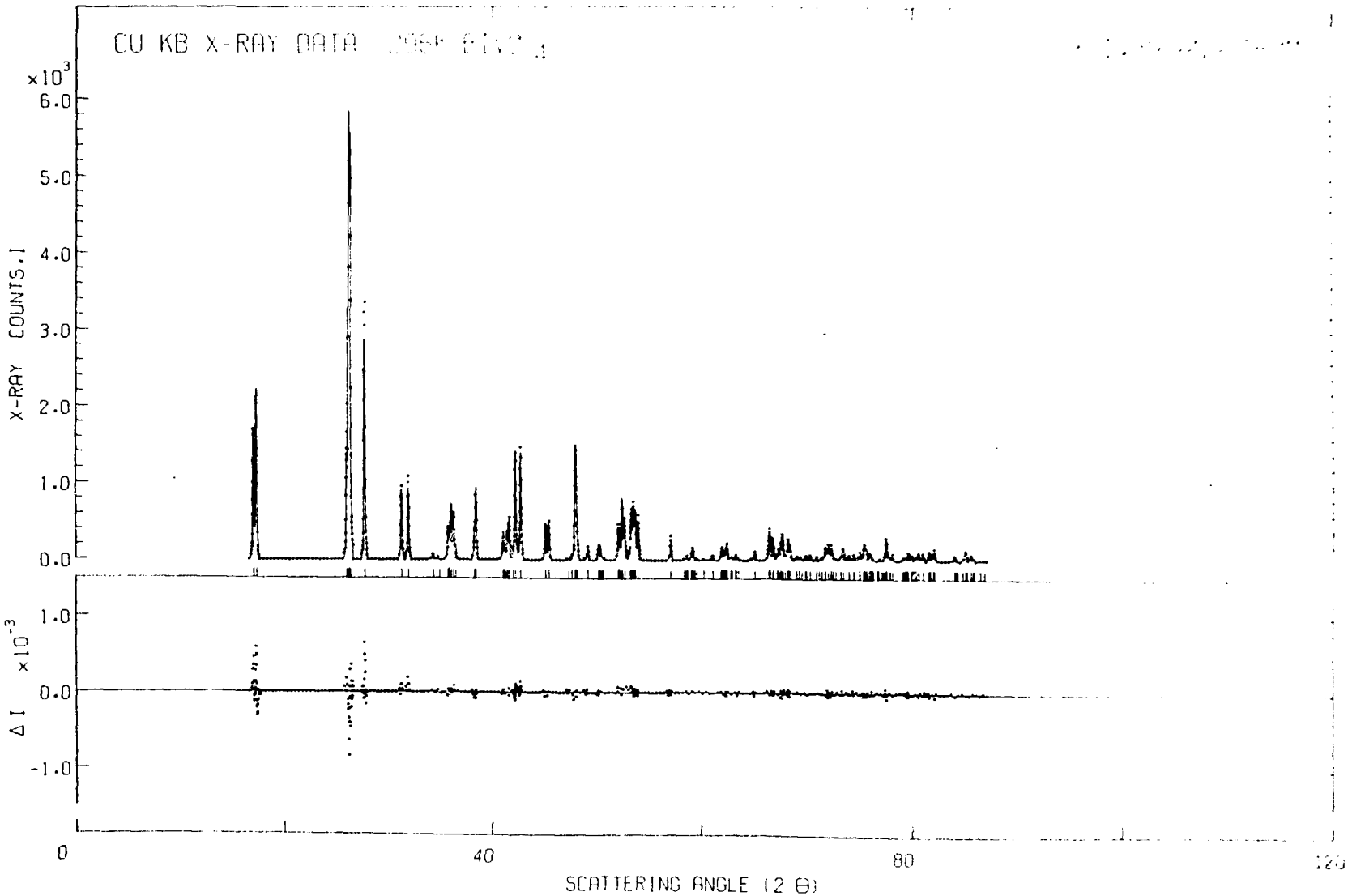
CU KB X-RAY DATA
×10^3
6.0
5.0
4.0
3.0
2.0
1.0
0.0
X-RAY COUNTS.I
1.0
0.0
-1.0
ΔI ×10^-3
0
40
80
SCATTERING ANGLE (2 θ)

FIGURE 7