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Nonuniform line broadening in high-pressure x-ray diffraction patterns

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Abstract. The powder patterns taken at high pressures with either a diamond-anvil apparatus or a tungsten-carbide-anvil setup occasionally exhibit unequal widths of the diffraction lines on the two sides of the direct beam. It is suggested that such a nonuniform broadening can arise if the incident x-ray beam passes through a region of large pressure gradient.

1 Introduction

Occasionally, the powder patterns taken at high pressure exhibit nonuniform broadening in that the diffraction lines of the same index (hkl) on the two sides of the direct beam have unequal widths, Figure 1 shows such a pattern of silver taken with a diamond-anvil apparatus. It is clearly seen that the diffraction lines on the left of the direct beam are much broader than the corresponding lines on the right. A similar effect is also noticed

(a)

(b)

Figure 1. A pattern of silver taken with a diamond-anvil camera (a) at high pressure-the nonuniform broadening is seen clearly-the lines on the left are much broader than the corresponding lines on the right of the incident beam-and (b) after the pressure was released to 1 atm; the nonuniform broadening disappears,

sometimes on patterns taken with a tungsten-carbide-anvil apparatus. This nonuniformity in line broadening disappears on releasing the pressure to 1 atm. A broadening of the diffraction lines is expected when the sample is squeezed between the anvils because of large microstrains, breaking-up of the coherently' scattering domains, and a host *of* other phenomena (Warren 1969). These factors, however, cause broadening *which* will in general be the same for a line, *(hkl),* on either side of the direct beam. In this paper we offer a possible explanation for nonuniform broadening in terms of pressure gradients in the sample.

2 Theory

The observed intensity profile of a powder line is given by the convolution of the profiles due to a large number of instrumental factors (Wilson 1963), and to factors which depend on the state of the sample (Warren 1969). It is customary to take the variance as a measure of the width of the line, because of convenience in mathematical operations introduced by the fact that the variance of a line profile is the sum of the variances of the component profiles. Because of certain simple geometrical concepts used later in the paper (figure 2), we shall take *full* width at half maximum, fwhm, as a measure of the width of the line profile, and for ease in mathematical operations assume the additivity of the fwhm of the component profiles. The additivity of the fwhm holds good only if the profiles have a Cauchy distribution: the general conclusions of this paper are not, however, affected by this assumption. As will be discussed later, the quantitative interpretation of the broadening may be affected by this assumption. For the present discussion we express as follows the fwhm of a line, *(hkl),* recorded after releasing the pressure to I atm,

$$W_O(hkl) = W_i(hkl)+W_s(hkl), \qquad (1)$$

where $W_s(hkl)$ is the width due to the finite area of the sample illuminated by the x-ray beam, and $W_i(hkl)$ is the total width due to all other sources.

The diffraction geometry encountered in a diamond-anvil camera (Bassett et al 1967) is shown in figure 2. AB defines the region of the sample illuminated by the incident x-ray beam. Let us assume that there exists a pressure gradient along AB when the sample is pressurised. For simplicity let us assume that A is at a higher pressure than B, and the pressure decreases monotonically from A to B. The

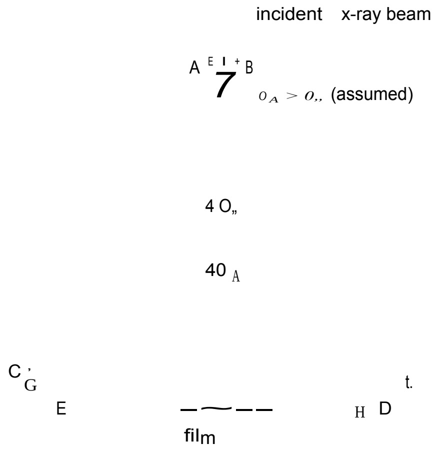

Figure 2. The diffraction geometry encountered in a diamond-anvil camera. GE = HF = W_5, and CG = HD = W_g.

diffraction angles for rays at A and B are denoted by B_A and B_B respectively, and $B_A > 6B$, because pressure at A is assumed to be higher than that at B. The diffraction angle decreases continuously on passing from A to B. As shown in figure 2, the rays diffracted from A strike the film at C and D,' and the. rays from B strike at E and F. The rays from all other points between A and B strike the film between C and t on' the left and between D and F on the right. Clearly, since $OA . > B_B$, CE > DF. Thus the widths due to the finite size of the region AB are not equal on both sides of the direct beam in the presence of a pressure gradient in the sample. The lines AG and AH are drawn parallel to lines BE and BF, respectively.

Since the change in 0 on application of pressure is small, to a good approximation we have the following results:

$$GE = HF - 2r\cos 20_{o}, = W_s, \tag{2}$$

where A\$ = 2r, and B_o is the diffraction angle at 1 atm. Further,

$$CG = HD = 2R(B_A - B_B) = W_g \tag{3}$$

Where W_g is the width arising from the pressure gradient, and R is the sample-to-film distance.

The total width of the line on the left of the direct beam is.given,bp

$$W_L = W; + W_p + W_g + W_s. \tag{4}$$

Similarly, the width on the right of the direct beam is given by

$$W_R = W, + W_p + I(W_S - W_g)I. \tag{5}$$

$W,$ *is* the broadening arising from the inhomogeneous stress component On release of pressure both W_g and W_p become zero.'

In practice, W_L, W_R, and Wo for a given reflection can be measured. Other parameters that can be evaluated with the help of equations (4) and (5) are given below.

Case I: $W_s > W_g$

$$2W_g . \_ W_L - W_R, \tag{6}$$

$$2W_p \quad W_L + W_R - 2W_o. \tag{7}$$

Case II: $W_S < W_g$'

$$2W, = W_L - W_R, \tag{8}$$

$$2W; = 2W_o - (WL - WR), \tag{9}$$

$$W_g + W_p = WL - WO- \tag{10}$$

It is seen from equations (6) and (8) that $(W_L - W_R)$ increases with increasing W_g initially, and becomes a constant equal to $2W_s$ for $W_g > W_s$.

The discussion so far has been confined to pressure gradients which vary monotonically in the region AB. In a diamond-anvil setup the pressure is maximum at the centre and drops to a value equal to the yield strength of the sample material at the edges. If the x-ray beam is considerably displaced from the region of maximum pressure, then a monotonically varying pressure gradient in the region AB (region 1 in figure 3) is encountered. For small deviations of the beam from the region of maximum pressure (region 2 in figure 3), the pressure first increases on passing from A to B, reaches a maximum at some point 0 between A and B, and then decreases. This case can be dealt with by considering the regions AO and OB separately and adding the widths. It is obvious that the region AO will produce a broadening such that $W_L < W_R$, and the region OB will lead to $W_L > WP$. An interesting case arises when AO = **OB.** Then $W_L = W_R$. This explains why W_L is equal to W_R where the incident x-ray beam is correctly aligned (ie it is situated symmetrically with respect to 0), even though the regions OA and OB are under a pressure gradient.

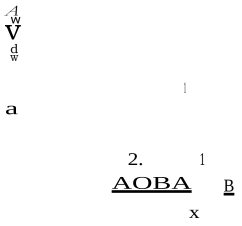

Figure 3. A schematic representation of the pressure distribution in the sample squeezed, between two diamond anvils. The x axis represents the line passing through the centre of the anvil face. Region 1: a monotonic variation of pressure between the points A and B is observed if the incident x-ray beam is displaced considerably. Region 2: pressure varies between points A and B for small displacements of the incident x-ray beam, increasing on passing from A to B, reaching a maximum at 0, and then decreasing.

3 **Experimental** results and discussion

A high-pressure pattern of silver (figure 1) which showed nonuniform broadening was chosen for the measurements of the widths W_L and W_R. Attempts to record the line profile with a microdensitometer were unsuccessful because of a very -poor peak-to-background ratio on the film. The widths of the reflections 111, 200, 220 and 311 were, therefore, measured with a low-magnification (x 5) microscope fitted with a micrometer. It must be noted that this method does not give fwhm, as defined. above and for this reason the present measurements can provide only a rough estimate of the various parameters.

The values of W_L and W_R and W_o for the reflections 111, 200, 220, and 3 11 are given in table 1. The values W_S, $2r$, W;, and $(W_g + W_p)$ derived from the values of W_L, W_R, and W_o on the assumption that $W_g > W_S$ are listed in table 2.

The average lattice strain causing a width W can be approximately calculated from the relation

$$\frac{Ad}{d} = \frac{W}{2R} \cot B.$$

Table 1. The results of the measurements on the diffraction patterns of silver shown in figure 1. Standard deviations are given in parentheses.

Number	hk1	W_L (cm)	WR (cm).	Wo (cm)
1	311	0·0850 (0·01)	0·0449 (0·006)	0·0390 (0·002)
2	220	0·0726 (0·006)	0·0311 (0·005)	0·0278 (0·003)
3	200	0·0695 (0·004)	0·0255 (0·002)	0·0275 (0·003)
4	111	0·0691 (0·006)	0·0202 (0·003)	0·0276 (0·003)
Mean'				0·0305 (0·006)

The pressure difference AP producing the broadening W can be estimated by c 'lculating the corresponding volume strain (AVIV) -3(M/d),and using the equation 'of state of silver (Rice et al. 1958). AP corresponding to 'W_g is the homogeneous pressure gradient across the line AB, while that corresponding to W_P is the average nonhomogeneous stress.... The average strains derived from (W_g +W_P) are also listed in table 2, and are nearly equal for the four reflections. The pressure difference between the points A and B'(figure 2) in this case is nearly 7 GPa, if $W_P = 0$ is assumed. This would mean a gradient- of nearly 500 GPa cm^{-1}. For a nonzero W_P, the gradient will be smaller than this. Such large pressure gradients are not uncommon in diamond-anvil squeezers. For example, if 20 GPa is reached at the centre of an 0.05 cm anvil, then the pressure gradient is nearly 800 GPa cm^{-1}.

The value of 2r derived' from W_g is 0·025 (0·001) cm as compared to the value of 0·015 (0·002) cm as obtained from the direct measurements. The figures between the parentheses are the standard deviations. The agreement between the two sets of values of 2r is reasonable in view of the fact that the measurements of W_L, W_R, and W_O are approximate. It is also possible that the condition $W_g > W_s$, assumed in this analysis, was not satisfied in the experimental setup used to record the pattern (figure 1). Thus, if W_g <. W_S is assumed, equations (6) and (7) can be used to estimate W_g and W_P respectively. These data indicate that W_g z- W_P. The pressure gradient estimated from Wg is nearly 270 GPa cm'. If W_g = W_F, is assumed in the previous case (W_S <, W_g), then a _pressure gradient of nearly 250 GPa cm^{-1} is obtained. Thus, whether Wg < Ws or $W_s < W_g$ is assumed, a similar order of pressure gradient is obtained.

Table 2. The various parameters calculated with the use of the data in table I and equations (8)-(10), on.the assumption that $W_g > W_s$.

hkl	W_S (cm)	2r (cm)	W; (cm)	$\frac{Ad}{d}$	$W_g + W_P$ (cm)	$\frac{Ad}{d}$
311 ,...;..	0·0200	0·0239	0·0104	0·0035	0·0545	0·0183
220	0·0207	0·0235	0·0097	0·0039	0·0421	0·0164
200	0·0235	0·0250	0·0070	0·0040	0·0390	0·0221
111	0·0244	0·0255	0·0040	0·0040	0·0386	0·0258
Mean		0·0245		0·0039		0·0207
Standard`... deviation		0·001		0·0002		0·004

4 Conclusion

It is shown that the nonuniform broadening often observed in high-pressure x-ray diffraction patterns can arise if, as a result of improper alignment, the x-ray beam passes through a region of large pressure gradient. The theory proposed here for the analysis of the line broadening has a drawback in that the additivity of the fwhm of the component profiles is assumed. The numerical values of the various parameters obtained for a specific case shown in figure 1 should be considered only approximate for two reasons: first, the additivity of fwhm assumed in the theory is not strictly valid and, second, the method employed for the measurement of the line width does not give strictly the fwhm.

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