

# X-ray diffraction line broadening of cadmium oxide produced by cadmium hydroxide decomposition

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A precise analysis of X-ray diffraction line broadening produced by cadmium oxide obtained by the thermal decomposition of  $\text{Cd}(\text{OH})_2$  is described. The influence of experimental conditions is considered. It is shown, using different methods of analysis, that the broadening of the reflections is due to size and microstrains effects, with a mean apparent size of 6 nm in a direction perpendicular to (1 1 0) planes.

## 1. Introduction

It has been shown that a detailed knowledge of the crystallite sizes of finely divided solids produced by a solid-state transformation gives useful informations about the structural transformation mode [1]. As is well known, an analysis of X-ray diffraction line broadening provides a non-destructive method for obtaining the bulk average of the size of coherently diffracting domains. In practice, the crystallite sizes should only depend on the reaction, and secondary phenomena, such as subsequent growth, must be avoided; this aspect was previously studied and discussed for cadmium oxide obtained by thermal decomposition of hydroxide [2]. It is also essential that two others aspects be carefully analysed: the broadening of the lines may be due to different effects and it is important to be sure of the reproducibility of the methods specially when changing the experimental conditions.

The present work is related to the decomposition of cadmium hydroxide into oxide and it will try to answer to the preceding questions. It is why a detailed analysis of X-ray diffraction line broadening of cadmium oxide produced by the chemical transformation has been undertaken.

## 2. Experimental details

### 2.1. Materials

Nine cadmium oxide samples were used for this work. Differences were in the origin of cadmium hydroxide; the reaction cell in which the decomposition is carried out and the temperature of the treatment. However, some experimental conditions were strictly respected for the preparation of these oxides:

1. the crystalline sizes of the three precursor hydroxides were always greater than those corresponding to the oxides produced, that is to say greater than the maximal critical sizes of the oxide crystallites [3].

2. to avoid subsequent growth of the oxide crystallites, it was necessary to carry out the reaction under a very low residual pressure of water vapour; for this, the reaction cell was always connected with a vacuum system using two liquid nitrogen traps. Furthermore the system has to be at temperatures lower than the critical temperature corresponding to the sharpening of the X-ray diffraction lines of the oxide [2]; it corresponds to the beginning of the crystalline defects resorption and/or to the intragranular sintering. Consequently, the decomposition reaction must

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TABLE I Origin and recording conditions of the X-ray diffraction lines for the nine CdO samples

Sample	Origin	Recording conditions
1	Cd(OH) <sub>2</sub> -C- MB Th <i>T</i> = 192° C	Siemens diffractometer CuK $\alpha$ -Filter: Ni Step scan: 0.02° 2 $\theta$ <i>I</i> peak = 11 000
2a	Cd(OH) <sub>2</sub> -A- R.D.H.T.A. <i>T</i> = 105° C	Philips diffractometer CuK $\alpha$ /graphite monochromator Step scan: 0.01° 2 $\theta$ <i>I</i> peak = 14 000
b	<i>T</i> = 150° C	
c	<i>T</i> = 190° C	
d	<i>T</i> = 280° C	
3a	MB Th <i>T</i> = 110° C Cd(OH) <sub>2</sub> A	CGR diffractometer CuK $\alpha$ /quartz monochromator Step scan: 0.02° 2 $\theta$ <i>I</i> peak = 200 000
b	<i>T</i> = 110° C Cd(OH) <sub>2</sub> C	
4	Cd(OH) <sub>2</sub> C MB Th <i>T</i> = 190° C	CGR diffractometer CoK $\alpha$ <sub>1</sub> /quartz monochromator Step scan: 0.02° 2 $\theta$ <i>I</i> peak = 22 000
5	Cd(OH) <sub>2</sub> C MB Th <i>T</i> = 190° C	Rigaku diffractometer CuK $\alpha$ <sub>1</sub> quartz monochromator Step scan: 0.02° 2 $\theta$ <i>I</i> peak = 12 000

be carried out with a very thin layer of hydroxide sample to avoid an increase of water vapour pressure into the layer [2].

The second column of Table I summarizes the origin of the nine oxide samples and experimental conditions. The various precursors were described in a previous work [3], they are reference here by the same letters A, B and C. The reaction decomposition was performed in a Mac Bain thermobalance (MB th) for samples 1, 3, 4, 5 and in a Rigaku Denki high temperature attachment (RDHTA) for sample 2.

## 2.2. Measurements

Table I gives the experimental conditions concerning the powder diffractometers used. The main difference is the wavelength range of the radiation. With a filter (sample 1) the two components  $K\alpha_1$  and  $K\alpha_2$  are present and an additional difficulty appears in the estimation of the background level [4–5]. In the case of a diffracted-beam graphite monochromator (sample 2), the  $K\alpha_2$  component is not eliminated but a better estimation of the background can be made. Finally, with an incident-beam curved-crystal monochromator the  $K\alpha_2$  component can be discriminated, the residual  $\alpha_2$  peak is usually about 1% of the  $\alpha_1$  (samples 3, 4, 5).

Corrections for instrumental and spectral broadening were made by means of data from CdO (BDH) annealed at 873 K for 36 h. Three measures of line breadth were used to study the broadening: the full width at half maximum (FWHM), the integral breadth and the Fourier analysis. The experimental data were corrected for polarization and the Lorentz factor and the background obtained by a least-squares procedure was subtracted. For this purpose it was assumed that the background varied linearly under each peak. Rachinger method [6, 7] was used to restore the  $K\alpha_1$  component when the doublet is present.

In order to correct the FWHM and integral breadth of the broadened profile  $h(s)$  for the contribution from the instrumental function  $g(s)$  it was assumed that the line profiles are of Gaussian or Lorentzian form [8]. Deconvolution of the experimental profiles in the Fourier analysis was carried out by the Stokes [9] and LWL [10, 11] methods.

## 3. Origin of line broadening in CdO

### 3.1. Preliminary analysis

The broadening of the diffraction peaks may be due mainly to size and microstrains effects. The simple method proposed by Williamson and Hall

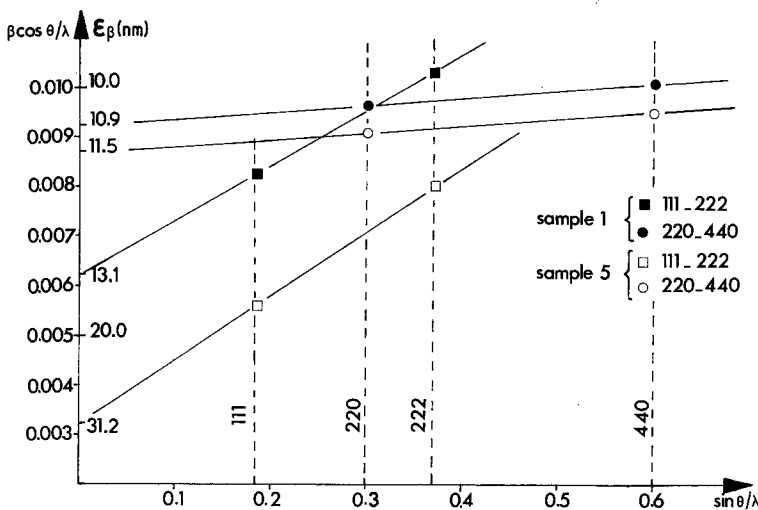


Figure 1 Williamson-Hall plot for CdO (samples 1 and 5), related to 111-222 and 220-440 lines (corrected with the Cauchy assumption).

[12] allows one to obtain an indication of the origin of the line broadening. The slope of the lines (Fig. 1) is related to the root mean square of lattice strains and the intercept depends on the mean size of the crystallites in a direction perpendicular to the planes being considered.

The results obtained from the pairs of lines 111, 222 and 220, 440 related to samples 1 and 5 are presented in Fig. 1, which has these main features:

(a) the mean size of the crystallites is smaller in the direction perpendicular to (110) than in the direction perpendicular to (111).

(b) the values of lattice strains obtained from the 220, 440 reflections are slightly smaller than the value deduced from 111, 222 pair.

(c) for the same pair of lines, the slopes are approximately the same for both samples.

(d) the mean sizes in a direction perpendicular to (110) are very close for both samples. It is not the case in the [111] direction.

It is necessary to note that there is a partial overlapping in the case of the 111, 222 pair, with 200 and 311 lines, respectively. It is not true for the 220, 440 couple. So, these results show that the broadening of 220 and 440 lines is mainly due to a size effect, with a slight strain contribution. A more detailed analysis of these lines has been undertaken.

### 3.2. Comparison between 220 and 440 profiles

It is well known that when there is no lattice strain, the Fourier transforms of two reflections,

in reciprocal coordinate,  $f_1$  and  $f_2$  related to two different orders must be identical. In practice, comparison between  $f_1$  and  $f_2$  profiles may be difficult, because it needs the previous deconvolution of the experimental broadened peaks  $h_1$  and  $h_2$ , respectively, by the "standard" profiles  $g_1$  and  $g_2$ . The latter represent the physical and geometrical aberrations of the diffractometer. The difficulties of this mathematical operation were pointed out by several authors [13, 14].

Also, it is impossible to compare  $h_1$  and  $h_2$  directly because  $g_1$  and  $g_2$  vary with the Bragg angle. Nevertheless, it is possible to avoid the deconvolution operation by the following process involving only well-defined convolution operations:

for the first order:  $k_1 = h_1 * g_2 = f_1 * g_1 * g_2$ ,

for the second order:  $k_2 = h_2 * g_1 = f_2 * g_2 * g_1$ .

As the convolution product is commutative, direct comparison between  $k_1$  and  $k_2$  is then possible. Identity of  $k_1$  and  $k_2$  implies the identity of  $f_1$  and  $f_2$  and consequently excludes the broadening partially or totally due to microstrains. If not, lattice distortions must contribute to the broadening of diffraction lines. To test this process, two experimental examples were chosen:

(a) The first one is related to a zinc oxide produced by the decomposition of  $Zn_3(OH)_4(NO_3)_2$  in which lattice distortions are negligible [15]. Fig. 2 shows the good agreement between  $k_{100}(s)$  and  $k_{300}(s)$  line profiles.

(b) The second one is related to 200-400 peaks of a cadmium oxide sample cold-worked by grinding [16].  $k_{200}(s)$  and  $k_{400}(s)$  are given in Fig. 3; the presence of microstrains in the oxide

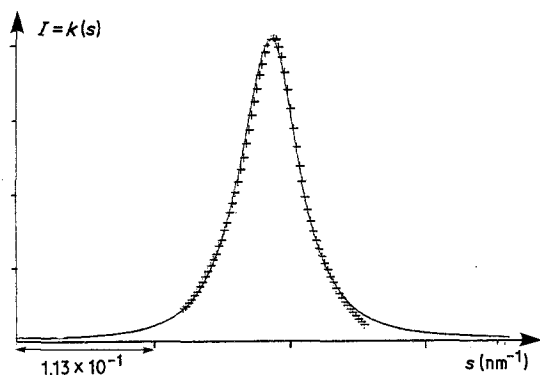


Figure 2 Direct comparison of  $k_{100}(s)$  (—) and  $k_{300}(s)$  (++++) line profiles of ZnO ex- $\text{Zn}_3(\text{OH})_4(\text{NO}_3)_2$ .

is responsible for the discrepancy between the two curves.

This rigorous approach, applied to sample 5 (Fig. 4) shows that the broadening of 220 and 440 diffraction peaks of CdO ex-Cd(OH)<sub>2</sub> is partially due to lattice distortions. The broadening of 220 and 440 experimental peaks is very important and is essentially due to a size effect.

This process gives only qualitative results; indeed, this method can be used in the case of large overlaps of the peaks (Fig. 5).

Such an approach gives basic information and could be extended for a quantitative determination of the microstrains when there is no substantial truncation of lines [17].

### 3.3. Evaluation of lattice strains

The determination of microstrains in CdO can be performed in a direction perpendicular to (110),

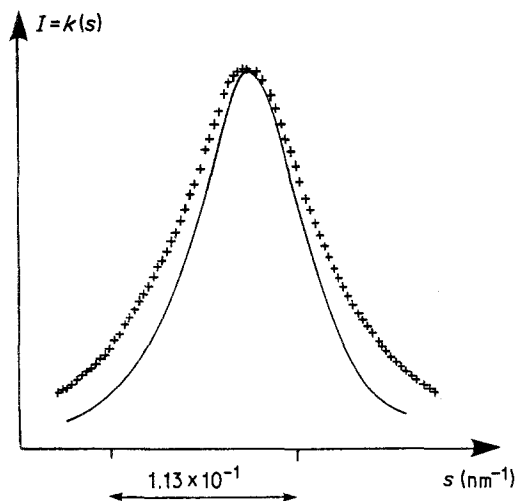


Figure 3 Direct comparison of  $k_{200}(s)$  (—) and  $k_{400}(s)$  (++++) line profiles of CdO cold-worked by grinding.

because the 220 and 440 lines are well resolved. The Fourier cosine coefficients  $A_n$  are normally expressed as a function of a distance  $L$  (nm) in the direction of the normal to the diffracting planes, when:

$$L = \frac{n\lambda}{2(\sin \theta_2 - \sin \theta_1)}$$

$\theta_2$  and  $\theta_1$  are the limits over which the line is recorded,  $\lambda$  the wavelength and  $n$  is the Fourier harmonic number. In practice a "hook" is usually observed for small values of  $L$  in the curve of  $A_L$  against  $L$ , due to an error in the estimated background level and the fact that profiles are necessarily truncated at a finite range. In this

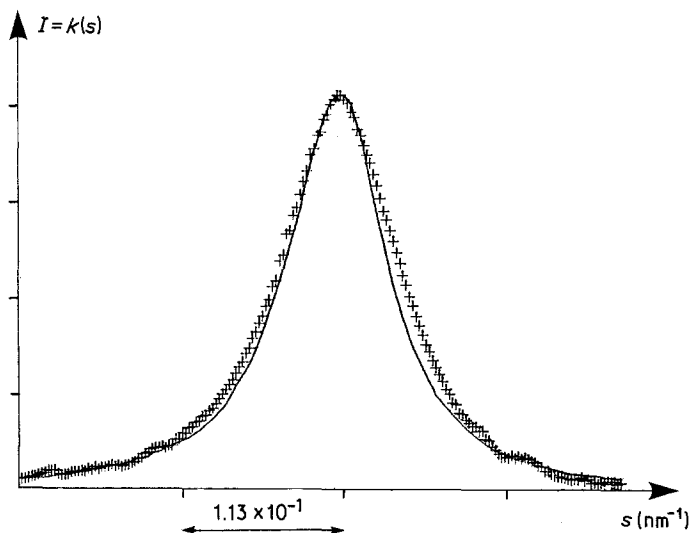


Figure 4 Direct comparison of  $k_{220}(s)$  (—) and  $k_{440}(s)$  (++++) line profiles of CdO ex-Cd(OH)<sub>2</sub> (sample 5).

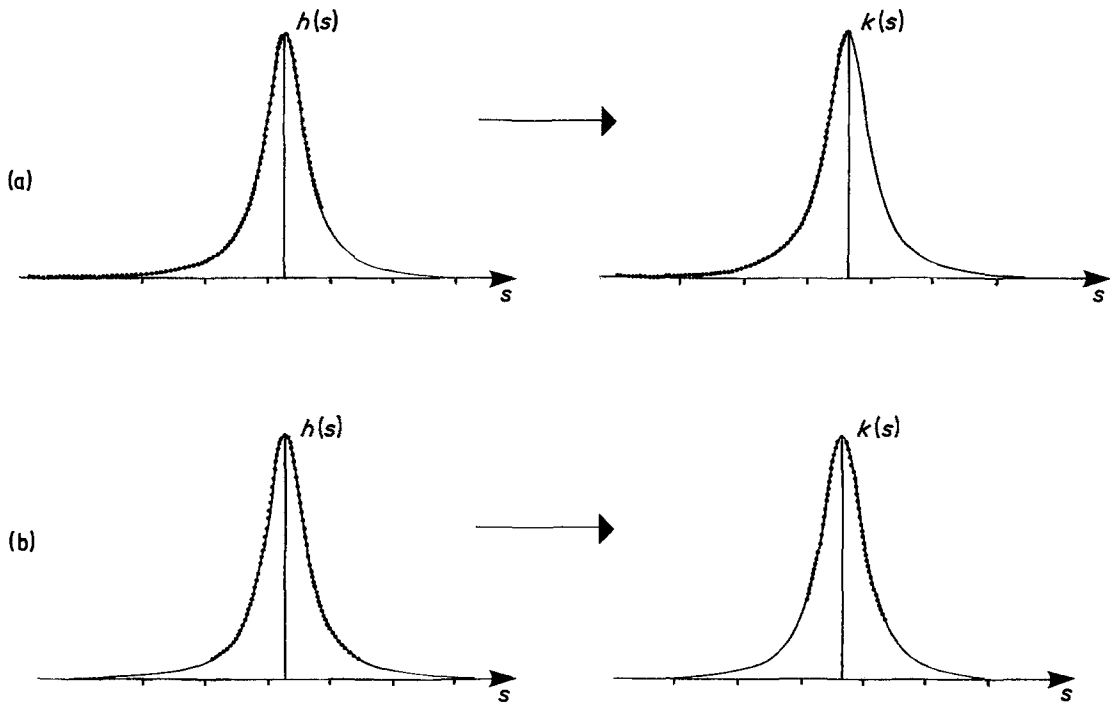
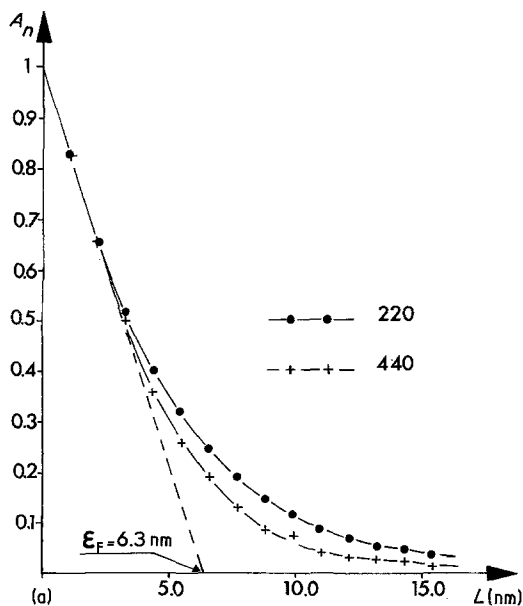


Figure 5 Direct comparison of two analytical line profiles with different orders when informations are lost due to overlapping. (—: whole profile; ·····: truncated profile).

analysis, allowance for the “hook effect” was made by means of the procedure suggested by Warren [18]. The origin of line profiles was chosen at the centroid. The  $A_L$  against  $L$  curves for the two reflections of sample 5 are given in Fig. 6a.

The Warren and Averbach method [19],



modified by Delhez and Mittemeijer [20], allows a separation of size and strain broadening; it is based on the different  $l$  dependencies of both contributions, through the relation:

$$A(n, l) \simeq A^S(n) - A^S(n) 2\pi^2 l^2 n^2 \langle e^2(n) \rangle$$

where  $A^S(n)$  is the size Fourier coefficient and

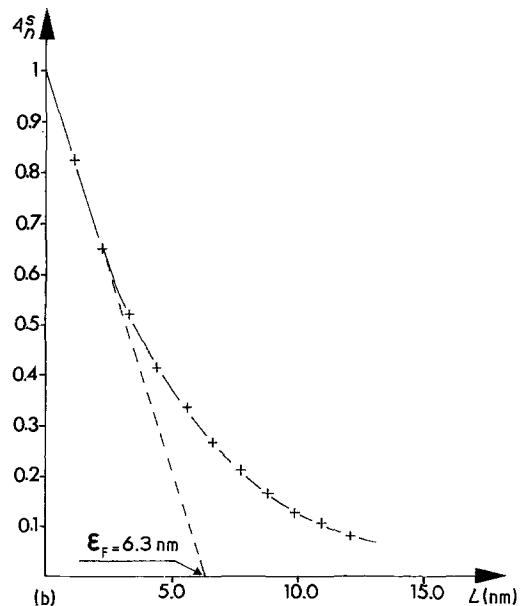


Figure 6 Fourier cosine coefficients  $A_n$  against  $L$  (a) and size coefficients  $A_n^S$  against  $L$  (b).

TABLE II Corrected breadths of 220 diffraction line for nine cadmium oxide.  $\omega$ : FWHM;  $\beta$ : integral breadth; the subscripts C, G denote that the parameter refers to Cauchy or Gaussian form assumption for the line; the subscript F denotes that the parameter is derived from Fourier analysis;  $\epsilon_F$  corresponds to the apparent size in a direction perpendicular to (110)

Sample	Line breadth ( $\text{nm}^{-1} \times 10^{-2}$ )						$\epsilon_F$ (nm)
	$\omega_C$	$\beta_C$	$\omega_G$	$\beta_G$	$\omega_F$	$\beta_F$	
1	6.93	2.96	9.73	10.95	7.53	10.89	5.6
2a	6.67	9.58	7.75	11.03	7.14	10.72	5.7
2b	6.57	9.35	7.64	10.85	7.14	10.53	6.2
2c	6.57	9.20	7.64	10.69	7.02	10.41	5.7
2d	6.57	9.22	7.64	10.72	7.08	10.48	6.1
3a	5.92	8.34	7.27	10.00	6.68	9.59	6.2
3b	6.12	8.78	7.58	10.45	7.25	10.46	5.9
4	6.16	8.34	7.36	9.90	7.02	9.91	6.2
5	6.42	9.12	7.31	10.24	6.97	10.39	6.3
mean value	6.44	9.02	7.57	10.54	7.09	10.38	6.0

$e(n)$  the strain. If two orders of the reflection are available,  $A^S(n)$  and  $\langle e^2(n) \rangle$  are readily evaluated from a plot of  $A(n, l)$  against  $l^2$ . The size coefficients for CdO (sample 5) are given in Fig. 6b. The root mean square strains  $\langle e^2(10 \text{ nm}) \rangle^{1/2}$  was evaluated at  $1.40 \times 10^{-3}$ . From the initial slope of the Fourier coefficient curve given in Fig. 6 very close values (6.3 nm) are obtained for the mean apparent size  $\epsilon_F$  in the [110] direction. An explanation for this situation can be found in the fact that it is realistic to consider that  $d[\langle e^2(L) \rangle]/dL$  ( $L \rightarrow 0$ ) = finite [21] and it is necessary to advocate also errors introduced by the "hook" effect correction, mainly for the 440 line due to the low intensity of this reflection.

In this study, the same 220 reflection was used for the various CdO samples, This line is well defined and the background can be well recorded on both sides. It was scanned for the nine samples for which origins and scanning conditions are described in Table I and the results are gathered in Table II.

The values obtained by the various methods applied to a same recording will not be compared and discussed, this was done elsewhere [21]. But for a parameter of dispersion used, the comparison of the results obtained for the nine samples is interesting. Within experimental error, reproducibility is good. This one must occur at two levels:

(i) Technical reproducibility, i.e. that which can be reproduced in recordings and in mathematical treatments\*. In fact, the recordings were intentionally done on a variety of diffractometers with various degrees of quality of the radiation. It is shown that the kind of equipment used plays a minor role if the reflections of the diffraction pattern are carefully recorded.

(ii) Reproducibility of physico-chemical phenomena; for the experimental conditions – temperature and water vapour pressure – mentioned in experimental part, it is observed:

(a) Firstly, the size  $\epsilon$  does not vary with the treatment temperature of the hydroxide. Thus, the sizes of the oxide crystallites obtained in these

\*The results, in Table II, related to samples 2a, 2b, 2c and 2d were obtained from four recordings which had already led to previous Table III in [1]. In this one, the mean sizes  $\epsilon_F$  were, respectively, 5.6, 5.7, 5.8 and 5.7 nm. The given values in these two tables are thus very closed even the treatments of the experimental intensities are noticeably different. Indeed, these recordings were achieved using the doublet  $K\alpha$  given by a graphite monochromator; in the present work, the Rachinger correction was used (leading to  $K\alpha_1$ ) before the deconvolution by Stokes method while, in [1], the deconvolution by the same method was achieved without the preliminary separation of the components  $K\alpha_1$  and  $K\alpha_2$ . This result agrees with the work of Kidron and Cohen [22] showing that a doublet separation is not required in Fourier analysis.

conditions are independent of the overall rate of the reaction. This result confirms previous works discussed elsewhere [1].

(b) Secondly, the size  $\epsilon$  is independent of the hydroxide sample used. This means mainly, that the sizes of the oxide crystallites do not vary with those of the precursor crystallites. Indeed, the precursor crystallite sizes must be greater than those of the oxide crystallites obtained; these results are in agreement with previous studies [3].

#### 4. Conclusion

This work shows that the results concerning the X-ray diffraction line broadening parameters of cadmium oxide are consistent. However, the preparation of CdO powder from the thermal decomposition of hydroxide has to be performed under closely controlled conditions, coupled with careful and systematic collection of diffraction data. It is shown that the semi-qualitative information which can be deduced very simply from a Williamson and Hall [12] plot forms a useful prelude to a more exacting analysis of size broadening. This method and the more precise analysis performed by direct comparison of line shape of different orders and by the Fourier procedure indicate that the line broadening of CdO ex-Cd(OH)<sub>2</sub> is due to size and microstrains effects. However the size effect predominates in the [110] direction; the corresponding apparent crystallite size is 6 nm. This value agrees well with the results described previously [1, 3] for cadmium oxide resulting from hydroxide decomposition.

#### Acknowledgements

The authors thank Dr N. H. Brett (University of Sheffield) for valuable discussions and the welcome of one of them (J. C. Niepce) in his laboratory.

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Received 19 May

and accepted 22 June 1983