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Structural aspects of ball milled CdS and CdSe

K. DUROSE, A. T. FELLOWS, A. W. BRINKMAN, G. J. RUSSELL, J. WOODS
Department of Applied Physics and Electronics, University of Durham, Durham, UK

The structural effects of ball milling powders of CdS and CdSe have been investigated by X-ray diffraction. When initially wurtzite-phase material was ball milled, excessive broadening and the selective extinction of certain diffraction lines were observed in Debye–Scherrer diffraction photographs of CdS and diffractometer traces of CdSe. These effects culminated in the disappearance of all but the three reflections from the (0 0 . 2), (1 1 . 0) and (1 1 . 2) planes. The fact that these reflections would coincide with those that would arise from the (1 1 1), (2 2 0) and (3 1 1) planes of the cubic sphalerite phase has led to earlier interpretations of similar effects in these and related materials as arising from a wurtzite to sphalerite transformation. Such a model does not fully account for the effects observed here. However, a careful examination of structure factors suggests an alternative explanation based on randomization due to structure deformation by faulting.

1. Introduction

It is well known that when hexagonal wurtzite zinc sulphide powder is subjected to grinding or milling, substantial changes in structure occur [1–3]. In general, these effects are manifested in X-ray diffraction as a progressive change from the expected wurtzite to a more cubic-like diffraction pattern. That is, the three closely spaced low-index diffraction lines normally observed from hexagonal ZnS are replaced by a single line and the (1 0 . 2) and (1 0 . 3) lines disappear completely [4]. Simultaneously there is also a great deal of line broadening [2]. These observations are usually interpreted as indicating a transformation from the hexagonal wurtzite to the cubic sphalerite phase [1, 3 4], although Smith and Hill [2] advanced an alternative explanation based on the randomization of the ZnS structure by deformation faulting.

This paper reports similar structural changes, as evidenced in the X-ray diffraction patterns, in ball milled powders of cadmium sulphide and cadmium selenide. These powders were intended for use in silk screen printing, either as low-cost thin-film solar cells or as thin photoconductive layers of CdSe in optically-latched displays. Ball milling was employed to reduce the powder particle size and improve the flow properties of the powder-paste during silk screen printing. The resulting work damage was annealed by a relatively short bake at about 500° C for both materials.

In spite of the growing use of CdS in silk screen printed solar cells, there have been few documented studies of the effects of ball milling on CdS and CdSe. However, structural changes of a similar nature have been reported in mechanically polished surfaces of single-crystal CdS, CdSe and ZnS by Russell *et al.* [4]. Using reflection high energy electron diffraction (RHEED) they observed the formation of cubic-like polycrystalline films on the surface of hexagonal single crystals of these materials, which they interpreted as the result of a mechanically induced transformation to the cubic phase. On the other hand, Takeuchi *et al.* [5] failed to detect any evidence for a cubic transformation in ball milled CdS after prolonged periods of ball

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milling, although there is evidence that the vigour and severity of the milling is more important than its duration [2].

2. Results

2.1. Ball milling of CdS

The cadmium sulphide was in the form of small crystalline platelets prepared from Optran grade CdS purchased from BDH Ltd (Poole, UK). Milling was carried out in a Temar swing mill. The colour of the CdS was observed to change from yellow through orange/yellow to orange/brown with milling, probably as a result of both work-damage and the reduction of particle size. Examination in the scanning electron microscope (SEM) revealed that the mean particle size had been reduced to $\sim 0.25\,\mu$m and that some agglomeration had occurred.

Fig. 1 shows the microdensitometer traces of a series of X-ray powder diffraction photographs taken from samples of CdS milled for 1, 6, 15 and 31 min. For comparison the microdensitometer trace of an unmilled, lightly crushed sample of CdS has been included. The sequence of results in Fig. 1 clearly shows that as milling proceeded a progressive change in the X-ray powder diffraction patterns took place. The first three hexagonal lines (1 0 . 0), (0 0 . 2) and (1 0 . 1) were replaced by a single line approximately coincident with the original hexagonal (0 0 . 2) line. The (1 0 . 2) reflection vanished as did the (1 0 . 3), although the (1 1 . 0) and (1 1 . 2) reflections remained. All lines of higher index also disappeared. After about 15 min milling only three significant X-ray diffraction peaks remained, so that the pattern more closely resembled that from cubic than that from hexagonal material. This was similar to the type of change widely reported for milled ZnS [1–3] and for polished CdS, CdSe and ZnS surfaces [4], which has usually been attributed to a transformation to the cubic phase. Under this supposition the three prominent remaining X-ray diffraction rings would index as the cubic (1 1 1), (2 2 0) and (3 1 1) respectively.

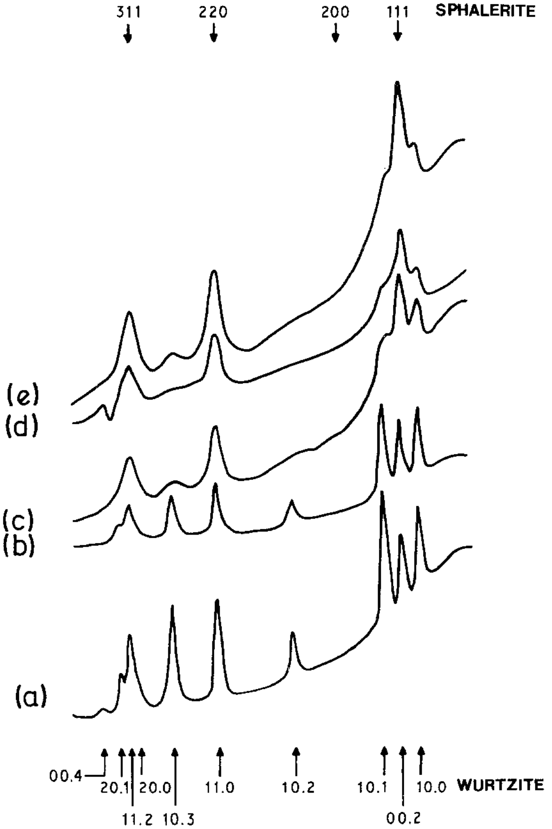

Figure 1 Microdensitometer traces of X-ray powder diffraction photographs of milled and unmilled CdS: (a) lightly crushed, unmilled CdS; (b) milled for 1 min; (c) milled for 6 min; (d) milled for 15 min; (e) milled for 31 min.

If a transformation to the cubic phase had indeed occurred, then it would be of interest to try and assess what proportion of the material had actually undergone such a conversion. In making this assessment, care must be exercised in allowing for the greater diffracting powers of cubic structures. A straight comparison of line intensities would be misleading by greatly exaggerating the proportion of cubic material. Since no calibration standard was available, calculations of diffraction intensity were carried out in an attempt to obtain an appropriate cubic/hexagonal intensity correction factor [6]. The comparison was made using the hexagonal (1 1 . 0)/cubic (2 2 0) line. The intensity of the hexagonal component of this line, as estimated from the (1 0 . 2) and (1 0 . 3) lines (which have interplanar spacings unique to the wurtzite phase) was subtracted from its measured intensity, and after correction the balance was taken to be the supposed cubic fraction. (The $I_{(11.0)}/I_{(220)}$ calculated intensity ratio was 1/8).

The change in the assumed cubic fraction (as determined above) with milling time is shown in Fig. 2. This suggested that after an initial increase during the first 8 to 10 min, the proportion presumed to have undergone the proposed transformation to the cubic appeared to saturate

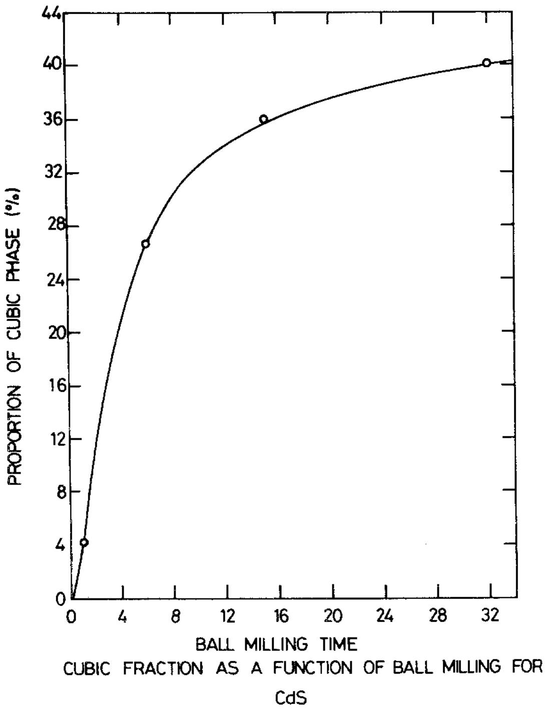

Figure 2 Variation in cubic proportion with milling time for CdS.

at about 40 to 50%. This may have indicated the establishment of some equilibrium mixture of phases. Alternatively it may simply have reflected the inability of the swing mill to inflict more than a given amount of damage. Interestingly, preliminary trials using a more lightweight Glen Chreston ball mill showed relatively little effect on the crystal structure after some 90 min of milling, and this may explain the discrepancy between these results and those of Takeuchi *et al.* [5] referred to earlier.

Finally, it was found that annealing milled powders of CdS at temperatures above 450° C apparently restored the hexagonal phase. X-ray powder diffraction photographs of powders which had been milled for 30 min and then annealed for 1 h in argon at 530° C indicated the complete restoration of the hexagonal structure. There was also a corresponding reduction in line widths to the natural width set by the instrumentation.

2.2. Ball milling of CdSe

The cadmium selenide powder was obtained from E. Merck (West Germany). As purchased, the powder consisted of small, rather angular grains, resembling crystalline platelets in shape. Milling was carried out in the Glen Chreston ball mill using tungsten ball bearings. Examination in the SEM revealed that the powder particles lost their angular appearance after two minutes of milling, becoming more rounded and spherical in shape. Particle size became more uniform and smaller. In unmilled powders, particle sizes ranged from about 5 to 50 μm, while after about 30 min milling the particle size range was ~ 0.1 to 0.5 μm. Fig. 3 shows a series of four X-ray diffractometer traces taken from unmilled CdSe and from CdSe milled for 2, 16 and 64 min respectively. These indicate that the X-ray diffraction spectra changed with ball milling in a similar manner to those of CdS.

The lines at 2θ values of 23°, 27° and 35° corresponding to the hexagonal (1 0 . 0), (1 0 . 1) and (2 0 . 1) reflections were progressively attenuated until only three strong reflections were left after 64 min milling. These were located at 2θ angles of 25.4°, 42.5° and 51° and could be indexed as being associated with the hexagonal (0 0 . 2), (1 1 . 0) and (1 1 . 2) or from the cubic (1 1 1), (2 2 0) and (3 1 1) planes, which would give a lattice parameter for cubic CdSe of 0.605 nm in close agreement with the estimate of 0.6052 nm made by Stuckes and Farrell [7].

As with CdS, the observed changes in the diffractometer traces could be interpreted as indicating a transformation of some of the material from the hexagonal to the cubic phase. If so, the proportion of the material undergoing the transformation can be estimated using the same procedure as for the CdS. Fig. 4 shows the variation in the assumed cubic fraction with ball milling time. Unlike the CdS, there does not appear to be any saturation, even after 64 min ball milling. However, this may have been because the Glen Chreston mill introduced much less damage than the Temar swing mill used for the CdS. The cubic fraction was only about 32% after 64 min milling, some 10% below the saturation level observed for CdS. Again, as for CdS the hexagonal phase was restored by annealing, typically for 2 h at 500° C in air.

2.3. Line-broadening effects

The diffractometer and microdensitometer traces (Figs. 1 and 3) revealed a considerable degree of line-broadening with ball milling. The variation in the full width at half maximum

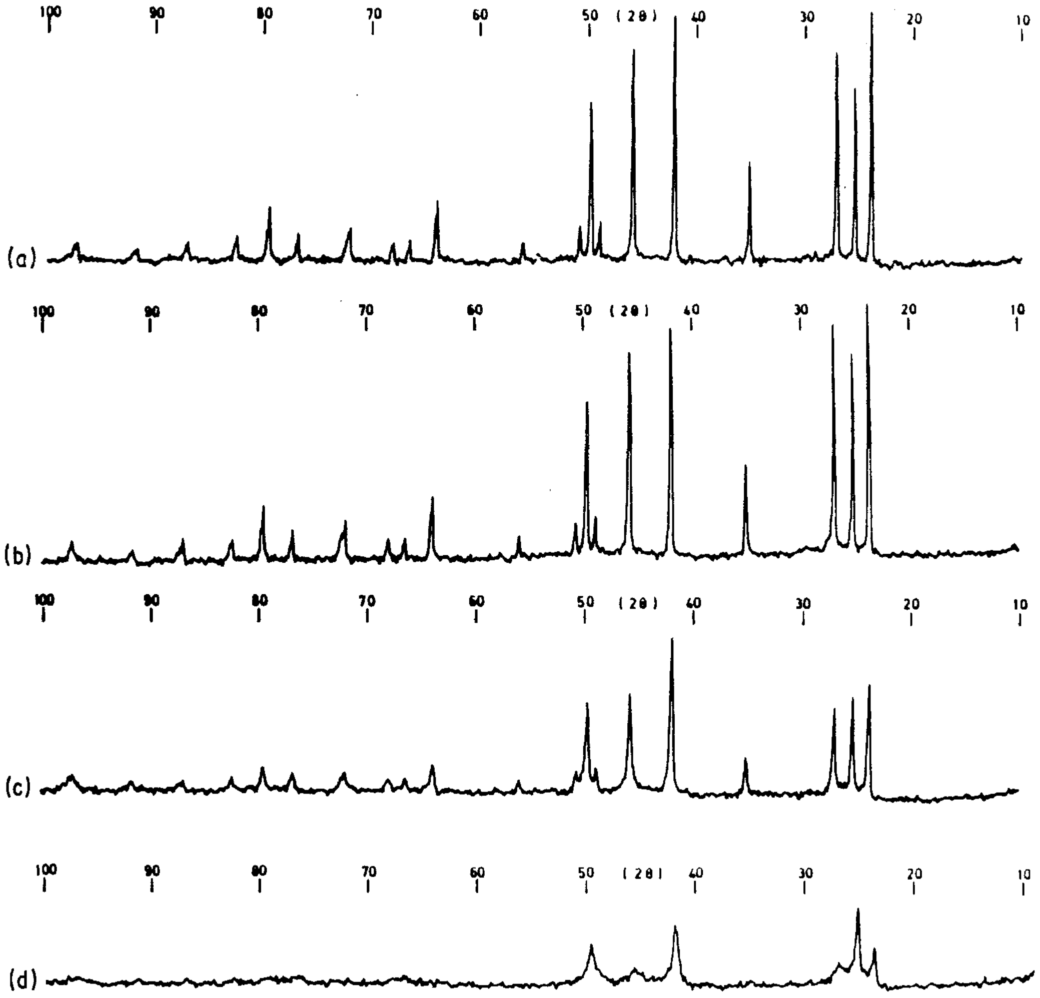

Figure 3 X-ray diffractometer traces of milled and unmilled CdSe powders: (a) unmilled CdSe; (b) milled for 2 min; (c) milled for 16 min; (d) milled for 64 min.

intensity for the (1 1 . 0)/(2 2 0) line of CdS and CdSe is shown in Fig. 5. In both materials there was a tendency for the line-broadening effects to saturate. With CdS the line width increased to a maximum of around 24 milliradians after about 15 min milling and remained constant thereafter. With CdSe, the line width was still increasing after an hour's milling, but sub-linearly (i.e. presumably saturation had not been reached at that stage). The apparent difference in the line-broadening of the two materials probably owed more to the fact that CdSe was milled in the more lightweight Glen Chreston mill rather than the heavy duty Temar swing mill, than to any property of CdSe. Of more importance was the observation that line-broadening was substantial in two compounds.

Line-broadening in X-ray diffraction is generally attributed either to particle-size effects or to non-uniform strain. The line-broadening observed here far exceeded that which might be expected from the effects of small particle size alone. Broadening on this scale would have required a reduction in particle size to ~ 10 nm, whereas examinations in the SEM showed that the minimum particle sizes were at least an order of magnitude larger. On the other hand, it would be very surprising if the particles were not severely mechanically damaged following ball milling. Thus, while some broadening may have been due to a reduction in particle size, the principal cause was probably due to strain arising from deformation faulting.

The similarity in the way that the line width increased with milling time and the way in which the apparently cubic fraction increased with

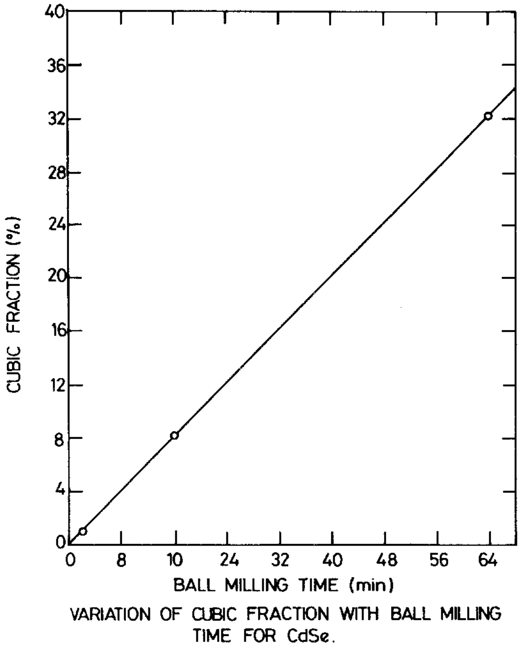

Figure 4 Variation in cubic proportion with milling time for CdSe.

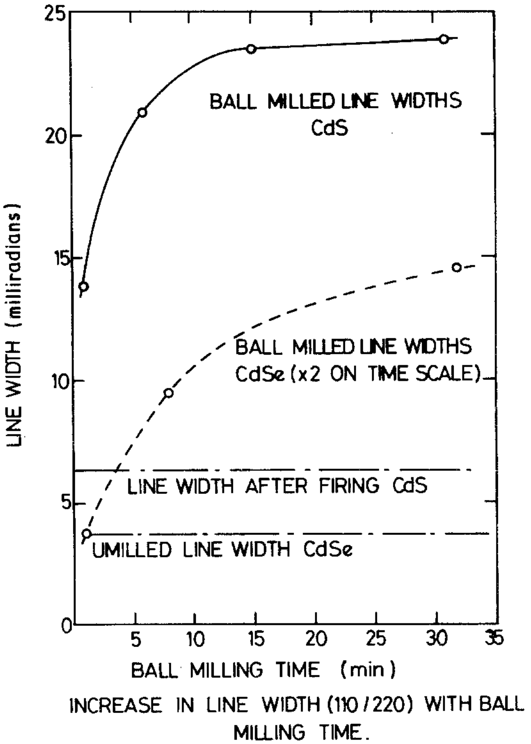

Figure 5 Variation in line width with ball milling time for both CdS and CdSe.

milling was particularly interesting, especially for CdS. It suggested that the two effects were closely related and probably depended on the degree of mechanical damage incurred during ball milling.

3. Discussion

The conversion of a hexagonal structure to a cubic one by a mechanical process such as ball milling must presumably depend upon the introduction of an appropriate stacking disorder through the movement of dislocations. In particular the passage of 1/3 ⟨21.0⟩ partial dislocations (which are usually designated as 1/6 ⟨211⟩ in the fcc system) over alternate (00.1) basal planes in an hcp structure will effect a transformation to fcc. Interestingly, this process is reversible and would be expected to lead to the establishment of some dynamic equilibrium between the proportions of cubic and hexagonal material. It would therefore be consistent with the shape of the graph of cubic fraction against ball milling time (Fig. 2) which saturated at about 40% cubic material.

Although such a model can in principle account for the change in the observed X-ray diffraction photographs upon ball milling, there are some conceptual difficulties. Principally, it is difficult to see how such a random and violent process as ball milling could introduce precise and specific dislocation movements. Undoubtedly dislocations are produced, but equally certainly their movements in general are not likely to be ordered. Indeed the substantial line broadening indicates the presence of considerable strain. More generally, it is difficult to understand how an ordered structure might be transformed to another ordered one (of higher symmetry), through the introduction of disorder.

A more serious problem was the total and consistent absence of a (200) diffraction line in the diffraction patterns from ball milled and cubic-like CdS. This particular line is weak when the difference between the atomic scattering factors of the metal and non-metal is small, and its absence from the diffraction pattern of ball milled CdSe was therefore not noteworthy. However, the greater disparity in the atomic scattering factors of cadmium and sulphur results in a much stronger reflection from the (200) planes in CdS. For example the ASTM powder file quotes the relative intensity of the (200) line at 40% for sphalerite CdS (Hawleyite). Yet the (200) diffraction line was never observed in X-ray diffraction photographs from ball milled CdS (or CdSe). Also absent was the

TABLE I Structure factors for sphalerite and wurtzite CdS

Wurtzite		Sphalerite	
hkl	$\|F\|^2$	*hkl*	$\|F\|^2$
10.0	$0.25\,(f_s + f_{Cd})^2$		
00.2	$4\,(f_S^2 + f_{Cd}^2)$	111	$16\,(f_s^2 + f_{Cd}^2)$
10.1	$1.5\,(f_S - 0.45\,f_{Cd})^2 + (1.67\,f_{Cd} - 0.866\,f_S)^2$	200	$16\,(f_S - f_{Cd})^2$
10.2	$(0.5\,f_S + 0.866\,f_{Cd})^2 + (0.866\,f_S - 0.5\,f_{Cd})^2$		
11.0	$4\,(f_S + f_{Cd})^2$	220	$16\,(f_S + f_{Cd})^2$
10.3	$(1.5\,f_S + 1.67\,f_{Cd})^2 + (0.45\,f_{Cd} - 0.866\,f_S)^2$		
11.2	$4\,(f_S^2 + f_{Cd}^2)$	311	$16\,(f_S^2 + f_{Cd}^2)$
20.1	$(1.5\,f_S - 1.67\,f_{Cd})^2 + (0.866\,f_S + 0.45\,f_{Cd})^2$		
00.4	$4\,(f_S - f_{Cd})^2$	222	$16\,(f_S - f_{Cd})^2$

somewhat weaker (2 2 2) diffraction line, and in fact the observed diffraction pattern was more similar to that of the diamond structure than that of sphalerite. Clearly, such an interpretation is not acceptable and therefore an alternative explanation must be sought

In a situation where the crystal lattice had been severely disrupted, all diffraction lines would suffer attenuation, while the diffuse X-ray background would increase. This was exactly what was observed (Figs. 2 and 4). However, attenuation would not be uniform across the diffraction spectrum, since some lines would be more affected than others. Consequently, the diffraction pattern would be changed dramatically. In trying to determine the net effect, some insight may be gained from an examination of the relevant structure factors. These were calculated for the low-index diffraction lines of the wurtzite and sphalerite phases, and the results are summarized in Table I. Apart from a constant factor (due to the different numbers of atoms in the wurtzite and sphalerite unit cells) the (0 0 . 2) and (1 1 1) reflections have the same structure factor, as do the other two pairs (1 1 . 0) and (2 2 0), and (1 1 . 2) and (3 1 1). These were, of course, the three principal diffraction lines remaining after ball milling and it is probably significant that their respective structure factors arise from simple sums of atomic scattering factors. It is arguable that these reflections are therefore the least likely to be affected by the introduction of disorder into the crystal lattice.

It is unnecessary therefore to postulate a phase transformation to explain the changes in electron and X-ray diffraction patterns from these materials. The observed differences may be understood simply as a consequence of increasing disorder. This is essentially the model suggested by Smith and Hill [2] to explain their observations. Of particular interest in their study were the results they obtained from grinding cubic zinc sulphide. In their material the (2 0 0) diffraction line was well resolved, and was used by them to measure line-broadening effects. This contrasts with our results where the reflection was totally absent in ball milled hexagonal starting material. The selective extinction of diffraction lines through mechanical damage is known to occur in other materials, notably metals where it is believed to arise from the effects of non-uniform and non-symmetrical deformation line-broadening [8].

If the observed changes in diffraction spectra do reflect just the randomization of structure rather than a true phase transformation, then the effects of the post-milling heating are easily understood as the annealing out of work-damage and not a reconversion back to the hexagonal phase. The kinetics of the cubic to hexagonal transformation in CdS have been investigated by Matsumoto *et al.* [9]. They found that at a temperature of 530° C, about 50% of a sample of cubic CdS was converted to hexagonal material in one hour and the proportion did not increase much for longer periods ($\sim$60% after 800 min). By contrast when the same treatment was given to ball milled CdS and CdSe, no trace of any cubic material was found in the resulting powder. This provides further support for the idea that the ball milling process led to a randomization of the structure rather than to a phase change.

In conclusion it may be noted that the absence of the (2 0 0) line from otherwise apparently cubic diffraction patterns is not, in fact, unique to ball milled CdS and CdSe. This diffraction ring was also absent from the RHEED patterns observed on mechanically polished crystals of CdS, ZnS and CdSe [4]. It was also absent from RHEED patterns taken from electrophoretically deposited films of CdS [10] and from CdSe single-crystal surfaces which had been aged in air [11]. In each instance the observed diffraction patterns have previously been interpreted as indicating the presence of the sphalerite phase. However, if the changes in the diffraction patterns do indicate a randomization of the structure then there are important implications for the action of air (i.e. oxygen) on single-crystal CdSe surfaces, and for the deposition of CdS films by electrophoresis where the grains appear to be formed in the sol with a highly disordered and imperfect structure.

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