

## Effect of mechanical grinding on the hexagonal structure of CdSe

Alessandra Geddo Lehmann

*Dipartimento di Fisica e INFN, Cittadella Universitaria, S. Prov. Le Monserrato-SESTU Km. 0.700, 09062 Monserrato (Cagliari), Italy*

Monica Bionducci

*Laboratoire Leon Brillouin, C.E. de Saclay 91191, Gif-sur Yvette cedex, France*

Franco Buffa

*Stazione Astronomica di Cagliari, Str. 54, Loc. Poggio dei Pini, 09012 Capoterra (CA), Italy*

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The wurtzite-sphalerite dimorphism of CdSe is studied by following the effect of high-energy mechanical grinding on the wurtzite form. X-ray powder-diffraction patterns are collected at different grinding times. A drastic modification in the initial wurtzite pattern is found already after 90 min grinding. The main effect is the progressive quenching of those Bragg reflections of wurtzite that are absent in the pattern of the sphalerite. A sphaleritelike pattern, with broadened peaks, results after 72 h grinding. Energy dispersive x-ray diffraction and differential scanning calorimetry both indicate the absence of any structural modification induced by thermal heating only. Two different models are proposed to describe the effect of grinding. The first one is a two-phase model for a transition from wurtzite to sphalerite. The second one, based on the concept of *latent parent structure*, hypothesizes a transition towards an hexagonal disordered structure. The two models are compared and discussed. [S0163-1829(98)03330-X]

### I. INTRODUCTION

The semiconductor CdSe, as many *II-VI* compounds, is dimorph at ordinary pressure. Depending upon preparation conditions, it crystallizes either as sphalerite (space group  $F\bar{4}3m$ ) or as wurtzite (space group  $P6_3mc$ ).<sup>1-3</sup> The most careful examination of the transition between the two forms established conclusively that the sphalerite is the stable low-temperature phase and that the cubic-to-hexagonal transition occurs at  $T_c = (95 \pm 5)^\circ\text{C}$ .<sup>4</sup> The preference of CdSe for the sphalerite was also found in a systematic study of binary *III-V* and *II-VI* octet compounds<sup>5</sup> in which a positive energy difference  $\Delta E_{\text{W-Sph}}^{\text{LDF}}$  between the hexagonal and the cubic structures was calculated by the local-density formalism. However, the energy difference is small (of the order of 2 meV/mol) (Ref. 5) and the wurtzite structure is retained, at room temperature, when samples are prepared at temperatures higher than  $T_c$ . The wurtzite-sphalerite polymorphism in CdSe has numerous practical consequences, among them being the modification of the properties of films for photovoltaic devices. As a result of the small energy difference and the moderate transition temperature, which is often near to the operating deposition conditions, such films may be composed by intimate intergrowth of cubic and hexagonal domains.<sup>6-8</sup>

Wurtzite and sphalerite are basic examples of adamantane structures (the term ‘‘adamantane’’ has recently been proposed by Parthé<sup>9</sup> for replacing the already adopted ‘‘adamantine’’) i.e., of structures that can be obtained by ordered atomic substitutions from the cubic and the hexagonal (*lonsdaleite*) modifications of diamond. They are in fact obtained by replacing in an ordered way (and conserving the mean valence electron number of four) one half of carbons by atoms of species  $T$  (say cations), one half by atoms of a dif-

ferent species  $T'$  (say anions), in such a way that in the resulting structures each  $T$ -type atom is tetrahedrally surrounded by four  $T'$ -type atoms and vice versa.

The two structures are strictly related from a geometrical point of view.<sup>1-3,9</sup> This is particularly clear when they are both referred to hexagonal axes (Fig. 1). In constructing the hexagonal cell of the sphalerite, the cubic [111] direction is taken as hexagonal [001], with hexagonal axes related to the cubic ones as  $c_h = \sqrt{3}a_c$  and  $a_h = (1/\sqrt{2})a_c$ . As can be seen, the two forms differ essentially for the packing along the ternary axis, which is of the kind fcc (i.e., *ABC*) in the sphalerite and hcp (i.e., *AB*) in the wurtzite.

It is the aim of this paper to discuss the modifications induced in the wurtzite structure of CdSe when polycrystalline samples are subjected to high-energy mechanical milling. Results will be compared with the effects caused by thermal heating only, this latter followed by *in situ* energy dispersive x-ray diffraction.

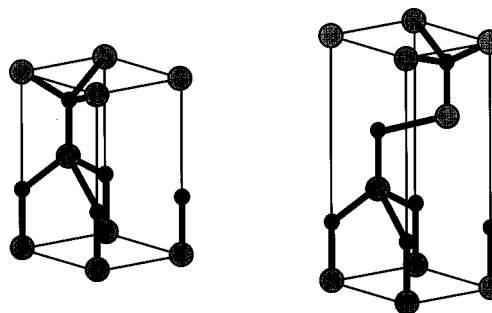


FIG. 1. Wurtzite (left) and sphalerite (right) structures referred to hexagonal axes. Se atoms are represented by large shaded circles and Cd atoms by small black circles. The cubic [111] direction of sphalerite is taken as hexagonal [001]. Hexagonal axes are related to the cubic ones as  $c_h = \sqrt{3}a_c$  and  $a_h = (1/\sqrt{2})a_c$ .

High-energy milling is one of the less conventional methods for inducing structural modifications in solids. In this process, powder of the starting material is subjected to highly energetic compressive impact forces in a ball mill. These impact forces result in repeated cold welding and fracture of the powder particles. Numerous experiments prove the efficiency of this process for obtaining not only crystal-to-amorphous transitions,<sup>10–12</sup> but also order-disorder transitions and metastable crystalline phases.<sup>13,14</sup> The driving force for the structural transformations observed during ball milling is still under discussion. Powder particles overheating, resulting from localized plastic deformation, has been sometimes suggested as the possible cause for the induced transitions.<sup>15,16</sup> However, different and more specific mechanisms have been successively explored.<sup>17,18</sup> These latter consider that severe plastic deformation generates, in the starting material, point and extended defects that rise the free energy of the initial structure. The basic premise is that, beyond a critical defect concentration, the structure will become unstable, which promotes a spontaneous structural change. As suggested in Ref. 19, under these assumptions structural changes during milling processes may have the character of catastrophic massive transformations and may be very different from structural evolution occurring under isothermal conditions.

## II. EXPERIMENT

Commercial polycrystalline hexagonal CdSe produced by Schuchardt was used in the experiment (99.999% purity). The process of mechanical grinding was carried out in a conventional planetary ball mill (Fritsch “Pulverisette”) using two cylindrical tempered steel vials of volume 220 cm<sup>3</sup>, each one filled with about 20 g of CdSe and 35 steel balls 1.0 cm in diameter, with a ball-to-powder ratio of approximately 1:8. To avoid oxidation, vials were sealed under pure argon containing less than 1 ppm oxygen. Milling was carried out with 10 min working and 5 min resting to avoid excessive warming of the vials. The rotating speed was kept constant at 250 turns/min. During milling, small quantities of CdSe were periodically extracted from one of the two containers for collecting x-ray diffractograms, while the second container was kept sealed to check the final result.

The maximum measured sample temperature after several hours milling was about 40 °C, but, as aforementioned, a local overheating of the powder during collisions cannot be ruled out. An estimation of the extent of the peak temperature reached by the powder particles can be obtained by using a simplified model already adopted in studying the system NiNb subjected to ball milling, for which a local increment of temperature  $\Delta T \cong 38$  °C was calculated.<sup>18</sup> Applying this same calculation to the case of CdSe, we can estimate a local temperature increment  $\Delta T \cong 32$  °C.

X-ray powder-diffraction patterns at different grinding times were collected with a D 500 Siemens diffractometer (Cu  $K\alpha$  radiation) equipped with graphite monochromator and rotating sample holder. Experimental integrated intensities were evaluated after automatic subtraction of background and  $K\alpha_2$  contributions.

Energy dispersive x-ray diffraction (EDXD) at different temperatures was carried out on the x-ray scanning diffrac-

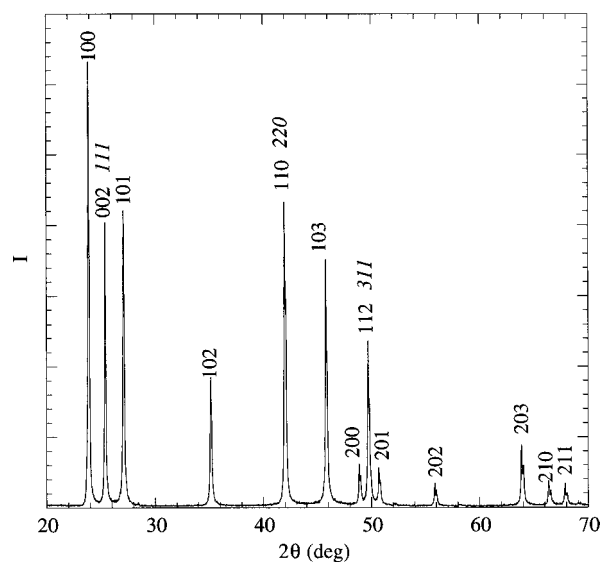


FIG. 2. Experimental x-ray powder-diffraction pattern of wurtzite CdSe. Miller indexes in italic letters are cubic indexes of those reflections that can also be assigned to the sphalerite form.

tometer previously described.<sup>20,21</sup> During measurement, samples were heated and kept under dynamical vacuum. The temperature was measured with a thermocouple in direct contact with the sample. Spectra were collected on the starting wurtzite powder and on the final products of grinding between room temperature and 255 °C, under isothermal conditions. Differential scanning calorimetry (DSC) was also performed (Perkin-Elmer calorimeter, 25 °C <  $T$  < 550 °C, heating rate 10 °C/min°) on the starting and final samples.

## III. X-RAY POWDER-DIFFRACTION RESULTS

### A. Effects of high-energy milling on hexagonal CdSe

The pattern of CdSe at the beginning of the experiment is shown in Fig. 2. Peaks are characterized by the sharpness of a well-crystallized powder and were completely indexed on a hexagonal cell with lattice parameters  $a = 4.31(1)$  Å and  $c = 7.02(1)$  Å, the values being in agreement with those reported in the literature for the wurtzite form of CdSe.<sup>4</sup> The relative intensities of Fig. 2 agree with those reported in the Joint Committee for Powder Diffraction Standard. This first pattern was assumed as the reference one for the wurtzite-type polycrystalline CdSe. In Fig. 2, cubic Miller indexes are also indicated, in italic letters, for those reflections that—for geometric reasons—can also be assigned to a sphalerite cell with lattice parameters related to the hexagonal ones as  $c_h = \sqrt{3}a_c$  and  $a_h = (1/\sqrt{2})a_c$  (see Fig. 1). The reason for this double indexation will soon be clear.

From top to bottom in Fig. 3, the reader can follow by visual inspection how the initial pattern is modified by the process of mechanical grinding. The reflections common to both wurtzite and sphalerite—those with double indexes in Fig. 2—are retained, while the Bragg intensities of those reflections that only belong to wurtzite rapidly decrease with increasing grinding time. This is particularly evident for the reflections  $(102)_h$  and  $(103)_h$ , which are quenched after only one hour and a half of grinding. This is in agreement with the well-known behavior of reflections with  $h-k$

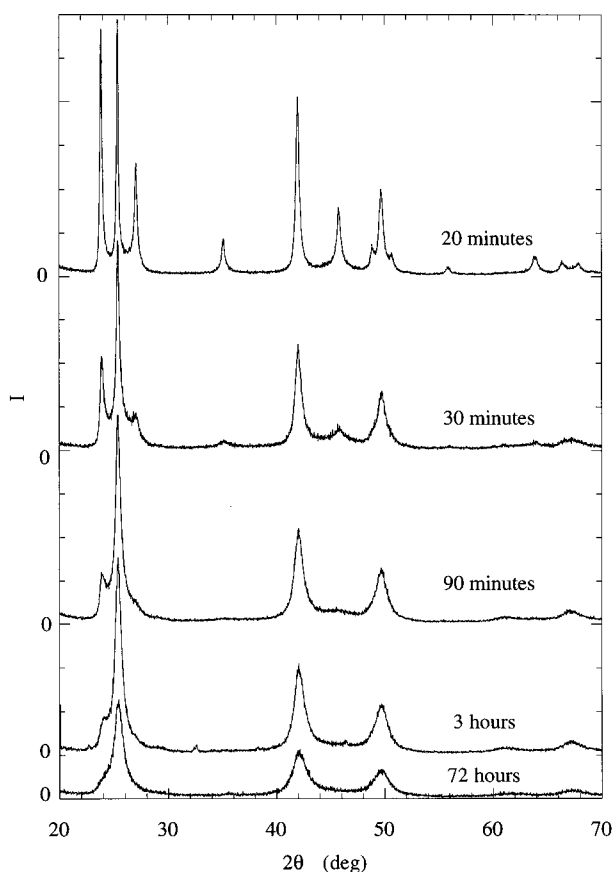


FIG. 3. Experimental x-ray powder-diffraction patterns of CdSe collected during mechanical grinding.

$\neq 3n$ , which, in a hcp structure, rapidly lose intensity with increasing stacking faults, while those with  $h-k=3n$  remain strong.<sup>22</sup>

In Fig. 3 it can be seen that, after 3 h grinding, small additional peaks are present, which can be ascribed to a small percentage of CdO due to air contamination. The reason why these peaks disappear in the following is likely due to increased background.

What remains after 72 h grinding is a sphaleritelike pattern. It contains just the reflections with hexagonal indexes  $(002)_h$ ,  $(110)_h$ , and  $(112)_h$ , shared with cubic symmetry as  $(111)_c$ ,  $(220)_c$ , and  $(311)_c$ . The observed broadening of Bragg reflections was expected as a consequence of the combined effect of diminished grain size and the presence of structural disorder within each grain, both induced by the mechanical treatment. No further modifications are observed in the diffraction pattern for grinding times longer than 72 h.

### B. Effect of thermal heating on CdSe

To ascertain to what extent the structural modifications shown in Fig. 3 can be ascribed to the specifics of the milling process, the effect of thermal heating was investigated by means of EDXD performed on the wurtzite CdSe powder, heated from room temperature to 255 °C. Different thermal cycles, characterized by different heating rates, were carried out. At the end, the sample was kept at 255 °C for twelve hours. As shown in Fig. 4, it is evident that no structural changes are induced in wurtzite CdSe just by thermal heating.

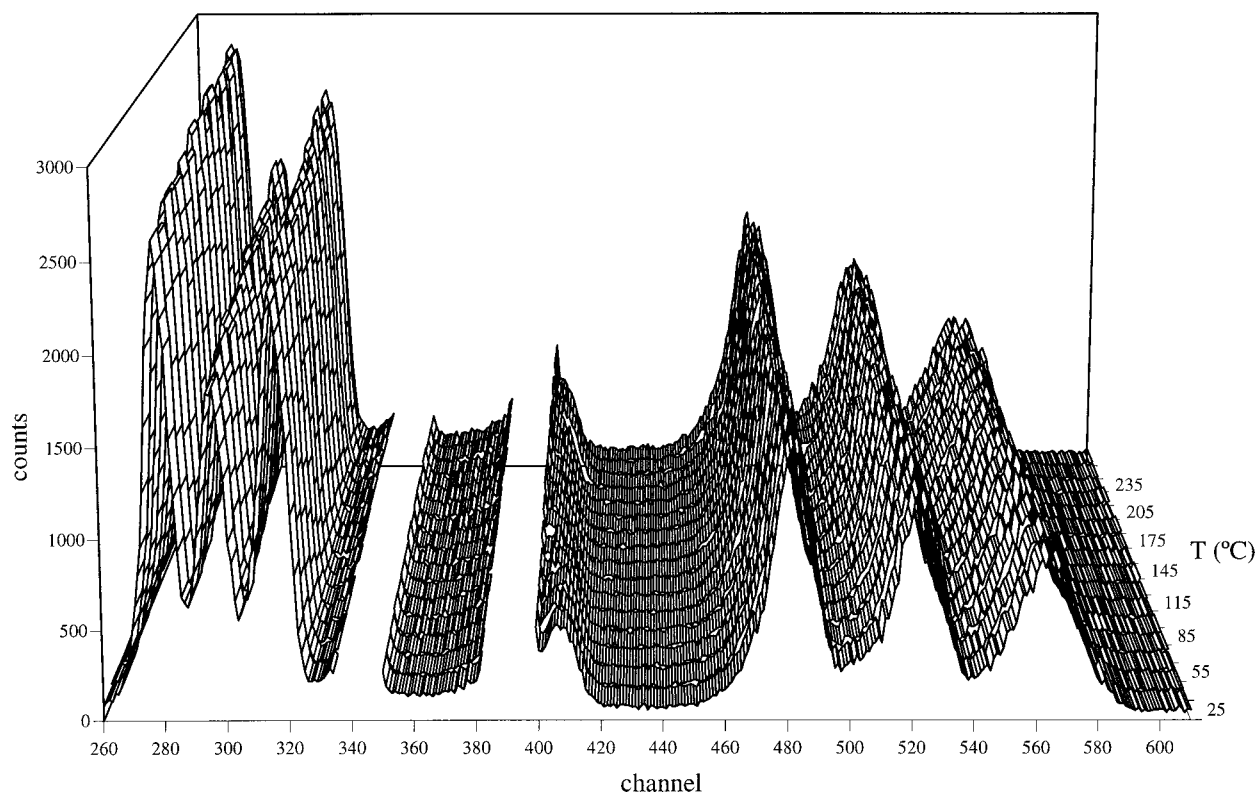


FIG. 4. Energy dispersive x-ray-diffraction patterns of wurtzite CdSe collected at different temperature during *in situ* thermal heating. Fluorescence peaks not belonging to the sample have been skipped out.

The same measurements were repeated on the final product of grinding. It was found that the mechanically induced modifications are retained, on heating, at least up to 255 °C and cannot be released by prolonged annealing at this temperature.

DSC analyses performed from room temperature to 550 °C, on both initial and final CdSe samples, showed once again no sign of structural changes induced by heating.

#### IV. DISCUSSION

The evolution of the x-ray powder-diffraction patterns as a function of grinding time indicates that important modifications have been mechanically induced in the wurtzite structure. Such modifications can, in principle, be studied by means of two different approaches.

The first approach is based on a two-phase model in which an increasing fraction of the initial wurtzite powder directly transforms into sphalerite during grinding. The hexagonal and the cubic phases coexist in the powder during the experiment. After 72 h all the wurtzite would transform into sphalerite.

The second approach hypothesizes a mechanically induced continuous order-disorder transition from the wurtzite to a final disordered structure. Such an approach is based on the concept of *disordered latent structure*. This concept has been used to model the cubic fcc $\leftrightarrow$ hexagonal hcp transformation as a transition between two low-symmetry ordered phases, which are both derived from a common *disordered hexagonal latent parent structure*.<sup>23</sup> This parent structure is a statistically disordered solid prototype, i.e., a phase composed by a disordered sequence of hexagonal close-packed planes.<sup>23</sup> According to this continuous model, the effect of grinding is to transform the wurtzite into the latent hexagonal structure.

Both approaches are significant. The geometry of the experimental patterns appears to represent a strong case in favor of the first one, that is to say in favor of a direct transition from wurtzite to sphalerite. Nevertheless, in our opinion the possible existence of the latent phase proposed by the second model must be checked in studying structures that present the wurtzite-sphalerite polymorphism, which is strictly connected with the hcp-fcc one. The concept of latent phase, developed in the theory of Dmitriev *et al.*<sup>23</sup> for hcp-fcc transformations in covalent and metallic structures, has been mainly used to support experimental results concerning metallic systems, such as mechanically ground cobalt;<sup>24</sup> but its relevance in the behavior of nonmetallic compounds like II-VI semiconductors cannot be underestimated.

To compare the previous models with the experiments, sequences of x-ray powder-diffraction patterns were simulated for the two cases. Simulations were carried out by LAZY PULVERIX.<sup>25</sup>

##### A. X-ray powder patterns simulation

*The two-phase model.* In the two-phase approach, the x-ray patterns are simply obtained by linear combination of the two patterns of wurtzite and sphalerite. Results are shown in Fig. 5. The relative amounts of the two phases, i.e., 40%,

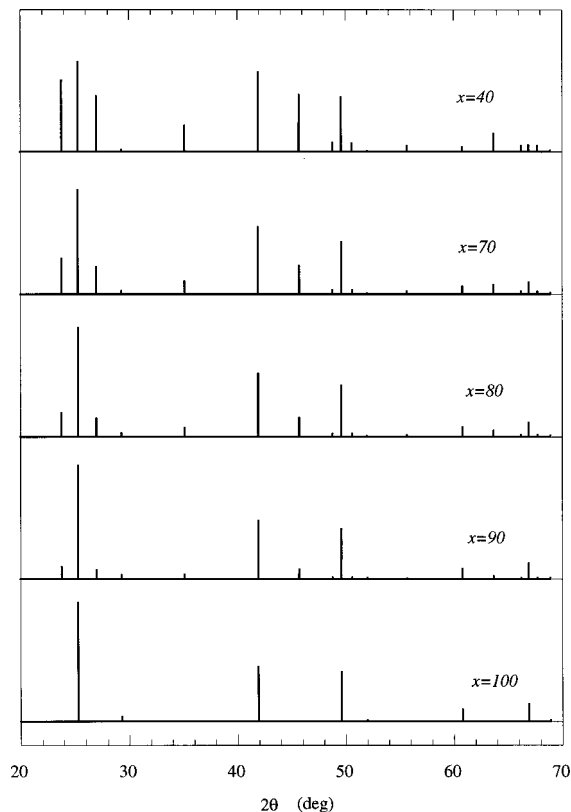


FIG. 5. Simulated x-ray-diffraction patterns for the two-phase model. Here  $x$  represents the percentage of sphalerite in the linear combination of sphalerite and wurtzite.

70%, 80%, 90%, and 100% sphalerite, reproduce the evolution of the experimental patterns as a function of grinding time.

*The continuous order-disorder model.* To give a description of the latent structure in the case of wurtzite and sphalerite, further insights on the connections between them are helpful. Figure 6 shows the (1120) plane for the two cells of Fig. 1. It can be seen that the two structures are the result of different stacking of a common slab, the height of which is equal to  $c_{\text{wurt}}/2$  and which contains one formula. The wurtzite is obtained by putting slabs in positions ABABAB of the close-packed arrangement, with the shortest repeated period equal to  $AB$  ( $=c_{\text{wurt}}$ ). The sphalerite is obtained by the sequence ABCABC..., with a repeated period equal to  $ABC$  ( $=\sqrt{3}a_{\text{sph}}$ ).

Different and more complex ordered sequences give rise to the so-called polytypes. More than 100 polytypes are known, for example, for SiC.<sup>9</sup> In such structures, stacking

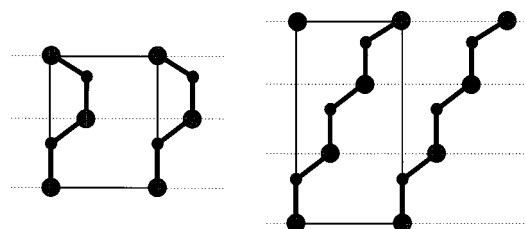


FIG. 6. (1120) planes for wurtzite (left) and sphalerite (right) structures referred to hexagonal axes. Se atoms are represented by large shaded circles and Cd atoms by small black circles (see text).

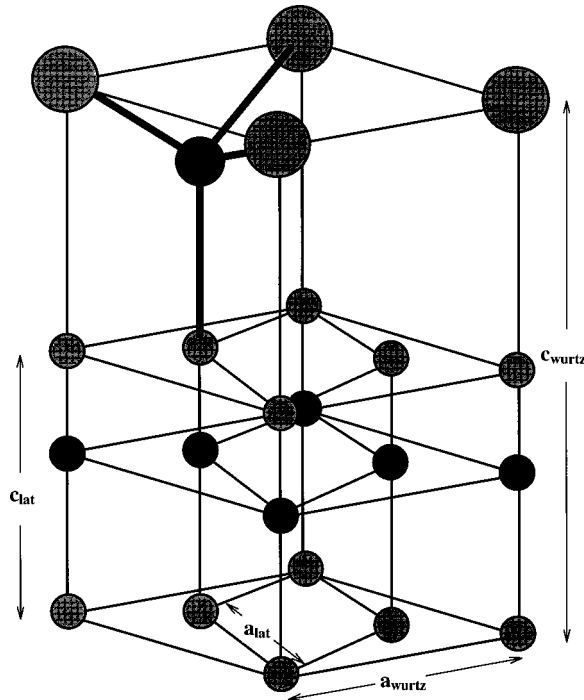


FIG. 7. Disordered latent structure depicted with respect to the ordered wurtzite. The latent structure is the small unit cell inside the large one. In the picture, only the lower one half of the wurtzite has been randomized into a latent structure. Fractional ( $\frac{1}{3}$ ) Se and Cd atoms are represented by the smaller shaded and black circles, respectively. Larger atoms belonging to the wurtzite have full occupancies.

faults, i.e., mistakes in the ideal sequence, are often present. A totally uncorrelated sequence of hcp slabs represent the disordered latent structure. The primitive cell of this structure, averaged over a large number of slabs—an average that corresponds to the space-time one performed by the x-ray probe—is depicted in Fig. 7. It has lattice parameters  $c_{\text{lat}} = c_{\text{wurt}}/2$ ,  $a_{\text{lat}} = a_{\text{wurt}}/\sqrt{3}$  that define a volume  $V_{\text{lat}} = \frac{1}{6} V_{\text{wurt}}$ . The symmetry is  $P3$  and the structure is composed by atoms in the following fractional positions: Se in  $0,0,0$  with occupancy  $\frac{1}{3}$  and Cd in  $0,0,\frac{3}{4}$  with occupancy  $\frac{1}{3}$ .

If the effect of grinding, during which, as mentioned, powder grains are squeezed between steel balls, is to introduce more and more stacking faults with increasing grinding time, then, as a consequence, each slab composing the wurtzite structure will get a probability different from zero, of being, at the same time, of types A, B, and C. The statistical sequence can eventually be realized. Partially disordered sequences would describe the effect of grinding while being within the first one hour and a half grinding time. Partially disordered structures have been obtained by constructing average cells intermediate between the wurtzite and the latent structure. In all these intermediate cases the cell of volume  $\frac{1}{6} V_{\text{wurt}}$  is no longer periodic. The suitable periodic parameters become  $a_{\text{part}} = a_{\text{wurt}}$ ,  $c_{\text{part}} = c_{\text{wurt}}/2$ , with  $V_{\text{part}} = \frac{1}{3} V_{\text{wurt}}$ .

Simulated x-ray powder-diffraction patterns in which an initial wurtzite CdSe gradually transforms into the latent structure are shown in Fig. 8. Pattern (a) corresponds to the wurtzite. Patterns (b) and (c) are calculated for the intermediate structures with atomic fractional coordinates and site

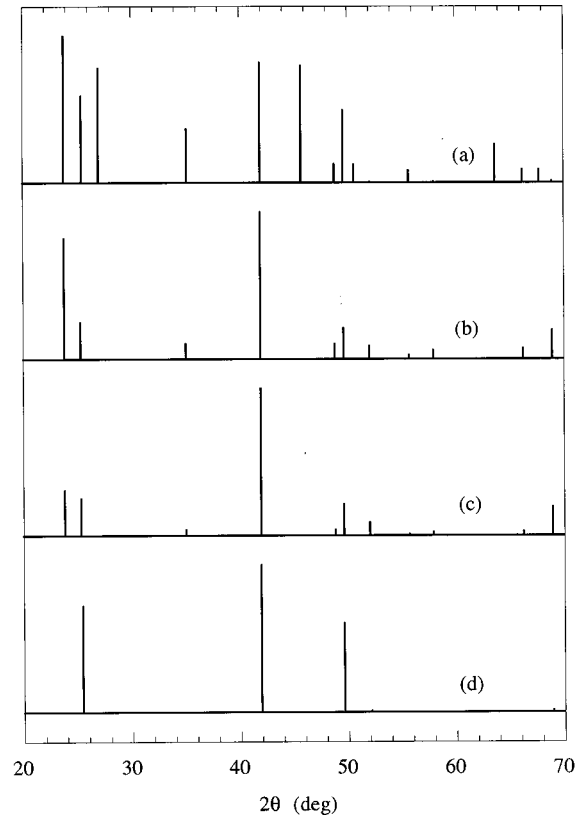


FIG. 8. Simulated x-ray diffraction-patterns for the continuous order-disorder model. (a): wurtzite; (b) and (c): intermediate structures defined in Table I; (d): latent structure.

occupancies defined in Table I. Pattern (d) corresponds to the limit case of all occupancies equal to  $\frac{1}{3}$ , coincident with the latent cell.

By comparing Figs. 3 and 8, it is clear that, in the simulation based on the latent structure, only the geometry of the experimental patterns after different grinding times is reproduced, while the relative intensities within each pattern are not. In particular, the intensities of the two first reflections at low angle are systematically inverted.

In contrast, the experimental intensities are better reproduced by the linear combinations of different fractions of wurtzite and sphalerite depicted in Fig. 5.

However, a more attentive inspection of some reflections suggests that neither the first nor the second model alone is sufficient for a satisfying description of the evolution of the experimental patterns. This can be seen in particular from

TABLE I. Partially disordered structures Occup. (b) and Occup. (c) used for obtaining simulated x-ray-diffraction patterns (b) and (c) of Fig. 7.

Atom	$x$	$y$	$z$	Occup. (b)	Occup. (c)
Se(1)	0	0	0	0.15	0.25
Se(2)	$\frac{1}{3}$	$\frac{2}{3}$	0	0.25	0.50
Se(3)	$\frac{1}{3}$	$\frac{1}{3}$	0	0.60	0.25
Cd(1)	0	0	$\frac{3}{4}$	0.15	0.25
Cd(2)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	0.25	0.50
Cd(3)	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{3}{4}$	0.6	0.25

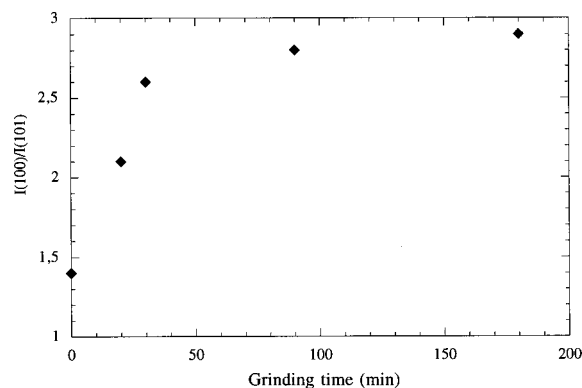


FIG. 9. Experimental integrated intensity ratio  $[I(100)/I(101)]$  as a function of grinding time.

reflections 100 and 101. As these reflections belong only to the wurtzite, the two-phase model predicts their integrated intensities ratio  $[I(100)/I(101)]_{\text{meas}}$  to maintain the constant value of 1.4, as it is in the wurtzite before milling. In contrast, the evaluated experimental ratio rapidly increases during the first 30 min and then saturates towards the value 2.9 (Fig. 9). A similar discrepancy is noted in the behavior of the two reflections, 110 and 112: the experimental intensities are in the ratio  $1.6 < [I(110)/I(112)]_{\text{meas}} < 2.0$  from bottom to top in Fig. 3, which is again not well reproduced in the two-phase model, according to which these two intensities would remain comparable. Concerning the final pattern, the three remaining experimental integrated intensities are in the ratios  $I_1 : I_2 : I_3 = 100 : 60 : 40$  (within 10%), to be compared with the simulated ratios 100:45:41 (sphalerite) and 72:100:60 (latent structure): the agreement with the sphalerite is just partial.

The measured intensities would be better reproduced by assuming a coexistence of both processes, i.e., the wurtzite-sphalerite transition and the creation of stacking faults in the wurtzite. In the special case of the aforementioned 100 and 101 reflections, the addition of an effect due to stacking faults formation would enhance more and more the simulated ratio  $[I(100)/I(101)]_{\text{simul}}$ , in better agreement with observations. The same is true for the agreement between  $[I(110)/I(112)]_{\text{meas}}$  and  $[I(110)/I(112)]_{\text{simul}}$ . Concerning the final pattern, it is easy to verify that a simulated phase mixture containing 15% of latent structure and 85% of sphalerite has intensities in the ratios  $I_1 : I_2 : I_3 = 100 : 56 : 46$ , more similar to the experimental ones.

## V. CONCLUDING REMARKS

The results of this study are interpreted as evidence of the contemporary presence of two effects induced in the wurtzite structure by high-energy milling: the first one is the wurtzite-to-sphalerite transition of CdSe, the second one is a contribution consisting in the progressive transition of a part of wurtzite towards latent structure. This second transition is continuous, in the sense that the wurtzite gradually transforms, via stacking faults, into the latent structure. As the latent structure is considered to be the prototypic phase for the wurtzite-sphalerite transition,<sup>23</sup> it might be argued that the process of formation of the cubic phase during milling actually takes place in two steps, passing through the formation of the hexagonal disordered phase. After 72 h milling, residual latent phase (an estimated percentage of about 15%) appears to be still present in the sample.

The described effects are ascribed to the special features of the milling process, as shown by the absence of structural modifications generated just by thermal heating. The effect of grinding is irreversibly retained after prolonged thermal annealing, at least up to the temperature of 255 °C.

A last point of discussion is the possible influence of impurities on the observed structural behavior. Iron contamination is unfortunately one of the most common and almost inevitable effects of ball milling. It is possible that the presence of iron is able to stabilize the sphalerite structure of CdSe, in the same way as iron impurities are known to stabilize the fcc modification in cobalt.<sup>24</sup> It is however difficult to say to what extent such impurities can influence the fine balance between the formation of stacking faults and the phase transformation toward sphalerite. Concerning the reflection broadening due to the mechanical treatment, the evaluation of the size effect and the disorder effect contributions to the linewidth is beyond the aim of this paper.

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<sup>1</sup>E. Parthé, *Crystal Chemistry of Tetrahedral Structures* (Gordon and Breach, New York, 1964).

<sup>2</sup>S. S. Devlin, in *Physics and Chemistry of II-VI Compounds*, edited by M. Aven and J. S. Prener (North-Holland, Amsterdam, 1967), p. 549.

<sup>3</sup>K. J. Siemsen and H. D. Riccius, *Phys. Status Solidi* **37**, 445 (1970).

<sup>4</sup>V. A. Fedorov, V. A. Gaushin, and Yu N. Korkishko, *Phys. Status Solidi A* **126**, K5 (1991).

<sup>5</sup>Chin-Yu Yeh, Z. W. Lu, S. Froyen, and Alex Zunger, *Phys. Rev. B* **45**, 12 130 (1992).

<sup>6</sup>R. Ludeke and W. Paul, *Phys. Status Solidi* **23**, 413 (1967).

<sup>7</sup>L. A. Sergeeva, I. P. Kalinkin, and V. B. Aleskovskii, *Sov. Phys. Crystallogr.* **10**, 178 (1965).

<sup>8</sup>M. F. Lawrence, N. Du, R. Philippe, and J. P. Dodelet, *J. Cryst. Growth* **84**, 133 (1987).

<sup>9</sup>E. Parthé, *Elements of Inorganic Structural Chemistry*, 2nd ed., edited by K. Sutter and E. Parthé (Petit Lancy, Switzerland, 1996).

<sup>10</sup>M. Bionducci, F. Buffa, G. Licheri, G. Navarra, B. Bouchet-Fabre, and J. M. Tonnerre, *Z. Naturforsch. Teil A* **51**, 71 (1996).

<sup>11</sup>E. Gaffet and J. P. Gaspard, *Colloq. Phys.* **4**, 205 (1990).

- <sup>12</sup>E. Gaffet, *Mater. Sci. Eng., A* **136**, 161 (1991).
- <sup>13</sup>A. E. Ermakov, E. E. Yurchikov, and V. A. Barinov, *Fiz. Met. Metalloved.* **52**, 1184 (1981).
- <sup>14</sup>E. P. Elsukov, V. A. Barinov, and G. N. Konygin, *Fiz. Met. Metalloved.* **62**, 719 (1986).
- <sup>15</sup>R. B. Schwarz, R. R. Petrich, and C. K. Saw, *J. Non-Cryst. Solids* **76**, 281 (1985).
- <sup>16</sup>E. H. Ellstern and L. Shultz, *Appl. Phys. Lett.* **48**, 124 (1986).
- <sup>17</sup>C. C. Koch and M. S. Kim, *Proceedings of the International Conference on the Structure of NonCrystalline Compounds, Grenoble, 1985* [*J. Phys. (Paris) Colloq.* **46**, C8-573 (1985)].
- <sup>18</sup>R. B. Schwarz and C. C. Koch, *Appl. Phys. Lett.* **49**, 146 (1986).
- <sup>19</sup>W. L. Johnson, *Prog. Mater. Sci.* **30**, 81 (1986).
- <sup>20</sup>M. Carbone, R. Caminiti, and C. Sadun, *J. Mater. Chem.* **6**, 1709 (1996).
- <sup>21</sup>V. Rossi Albertini, L. Bencivenni, R. Caminiti, F. Cillocco, and C. Sadun, *J. Macromol. Sci., Phys.* **35**, 199 (1996).
- <sup>22</sup>A. Guinier, *Théorie et Technique de la Radiocristallographie* (Dunod, Paris, 1964), pp. 541–560.
- <sup>23</sup>V. P. Dmitriev, S. B. Rochal, Yu M. Gufan, and P. Tolédano, *Phys. Rev. Lett.* **62**, 2495 (1989).
- <sup>24</sup>F. Cardellini and G. Mazzone, *Philos. Mag. A* **67**, 1289 (1993).
- <sup>25</sup>LAZY PULVERIX, a program to calculate theoretical x-ray and neutron powder diffraction patterns, by K. Yvon, W. Jeitschko, and E. Parthé.