PHYSICAL REVIEW B VOLUME 58, NUMBER 21 1 DECEMBER 1998-I

High-density phases of ZnO: Structural and compressive parameters

Serge Desgreniers
Département de Physique, Université d'Ottawa et Institut de Physique Ottawa-Carleton, 150 Louis Pasteur, Ottawa, Ontario, Canada K1N 6N5

(Received 2 June 1998)

Dense ZnO phases, obtained by static compression at room temperature, are studied by x-ray diffraction using synchrotron radiation. The initial wurtzite structure of ZnO is observed to transform to the rocksalt structure at 9.1 ± 0.2 GPa with a large volume collapse of 16.7% on increasing pressure. Accurately determined structural and compressive parameters over a large pressure range for both phases are presented. We report the following values for the null compression bulk moduli and their pressure derivatives: 142.6 GPa and 3.6 and 202.5 GPa and 3.54, for the wurtzite and the rocksalt phases, respectively. From a comparison between the present results and calculated ones, it is inferred that Hartree-Fock calculations yield the best estimation of the compressive parameters in dense ZnO. Furthermore, we show that the ideal relationship between the c/a axial ratio and the u oxygen positional parameter is preserved as the wurtzite lattice becomes denser while approaching the structural transition pressure. [S0163-1829(98)04945-5]

I. INTRODUCTION

Synthetic ZnO is used in numerous applications, for instance, as a chemical sensor, a catalyst, and for the fabrication of optical thin coatings. Natural ZnO represents an analog for important constituent phases of the lower mantle.[1] Contrarily to other IIB-IVA binary compounds which adopt different metastable structures, bulk zinc oxide is known to crystallize only in the hexagonal wurtzite structure ($P6_3mc$, $Z=2$) at room conditions. A transition to the cubic rocksalt structure ($Fm3m$) takes place at room temperature at around 9 GPa resulting in an increase of coordination number, from 4 to 6, and a large volume decrease of about 17%.[2] The ionic component of the tetrahedrally covalent bonding of the wurtzite structure of ZnO leads to a transformation to the rocksalt structure, as it is the case for other IIB-IVA binary compounds. Apart from a recent study of Gerward and Staun Olsen,[3] structural and compressive data obtained with the latest x-ray diffraction techniques using synchrotron radiation in a pressure range well beyond the wurtzite-to-rocksalt transition pressure are not available. Although the wurtzite-to-rocksalt transition had been recorded, other studies had covered a smaller pressure range.[2,4]

New computational techniques have led to calculations of the compressive properties of simple solids. Several computational studies have been reported on the physical properties of dense ZnO.[4–7] A critical comparison between experimental and theoretical results is possible for ZnO as the structural and compressive parameters can be measured with a fair level of accuracy since the dense solid adopts simple structures. The goal of the present high pressure x-ray diffraction study of ZnO is threefold. First, measure by energy-dispersive x-ray diffraction using synchrotron radiation accurate equations of state, the pressure dependence of relevant structural and compressive parameters of both the low pressure wurtzite and the high pressure rocksalt phases. Second, compare the experimental results with recent calculated compressive properties. Third, study the pressure-induced change of the u oxygen positional parameter for the wurtzite structure.

II. EXPERIMENT

Polycrystalline ZnO with a nominal purity of 99.99% was obtained from Alfa AESAR. Both *in situ* x-ray diffraction using a Bragg-Brentano diffractometer and micro-Raman spectroscopy indicated that no detectable crystalline phases other than the wurtzite phase were present initially at room conditions in the sample. Measured lattice parameters of the starting material at room conditions, $a=3.2498$ Å, $c=5.2066$ Å, and $c/a=1.6021$, were in close agreement with the published data or with those of NIST ZnO certified x-ray diffraction standard.[3] Ground samples were loaded in a gasketed diamond anvil cell using silicone fluid (Dow Corning 200) as a pressure transmitting medium, generating pressures in excess of 50 GPa. Fine Cu powder, mixed with the sample, was used as a pressure gauge. Our pressure calibration (pressure-volume interpolation) was based on available shock compression data of Cu reduced to 300 K isothermal $P(V)$ data[8–10] and fitted to the third-order Birch-Murnaghan equation of state $P(V)=(3B_0/2)[(V/V_0)^{-7/3}-(V/V_0)^{-5/3}]\{1+\frac{3}{4}(B_0'-4)[(V/V_0)^{-2/3}-1]\}$, with $B_0=129.5$ GPa and $B_0'=3.35$. Pressure variations across the probed area lead to an increase of diffraction line linewidth less than the broadening due to strain induced by grain boundary interactions.

Energy-dispersive x-ray diffraction experiments (EDXD) were performed at the National High Pressure Facility of the Cornell High Energy Synchrotron Source (CHESS/B1 line).[11] Appropriate white x-ray beam collimation was provided by crossed microslabs of tungsten defining a nearly square 900 μm^2 beam. The Bragg angle calibration was obtained from x-ray diffraction of a thin Au foil, accurately located at the sample position. All EDXD spectra were acquired at $Ed=40.28\pm0.05$ keV Å. X-ray diffraction spectra were analyzed (the line profile fitting and lattice parameter refinements) using program XRDA.[12,13]

©1998 The American Physical Society

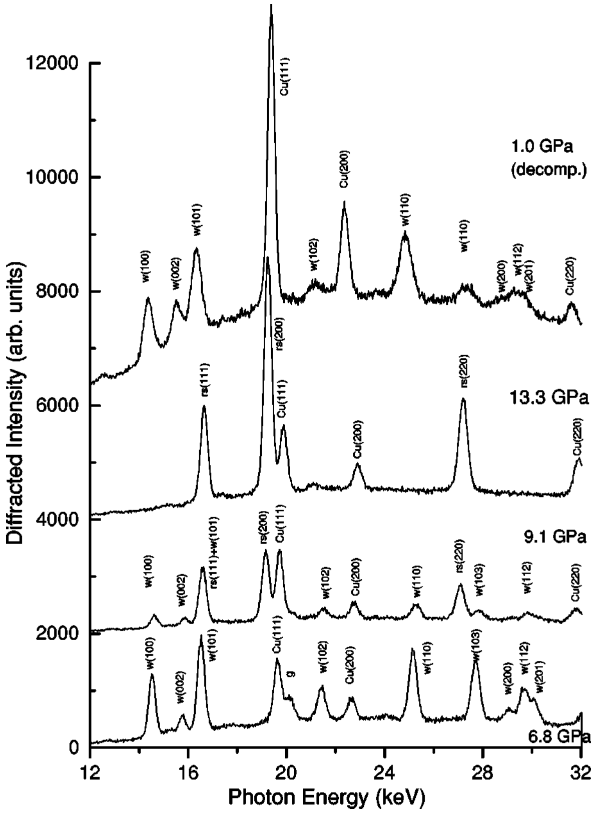

FIG. 1. Examples of EDXD spectra indicating the coexistence of the wurtzite and rocksalt phases around 9.1 ± 0.2 GPa (increasing pressure) and the emergence of the wurtzite phase $P \leqslant 1.9$ GPa ± 0.2 GPa upon decompression. For all spectra $Ed \simeq 40.3$ keV Å. Spectra are presented in cascade for clarity. Labels w and rs refer to wurtzite and rocksalt, respectively. X-ray diffraction lines from the Cu pressure gauge and the gasket material are labeled as Cu and g, respectively.

III. RESULTS AND DISCUSSION

A. The wurtzite-rocksalt structural transition

A large number of EDXD spectra were recorded at pressures ranging from 0.1 MPa to 56 ± 1 GPa at room temperature with increasing and decreasing pressures. A clear wurtzite-to-rocksalt transition is observed starting at 9.1 ± 0.2 GPa with increasing pressure. The two phases coexist over a pressure range of 9.1 to 9.6 GPa, as shown in Fig. 1. The structural transition is complete at 9.6 GPa resulting in a drastic 16.7% change in the unit cell volume. Our result for the wurtzite-to-rocksalt transition pressure is in close agreement with those reported in previous studies.[2–4] The high pressure rocksalt phase is stable up to 56 ± 1 GPa, the highest pressure achieved in the present study. ZnO is predicted to transform to the CsCl-type structure as it is the case for larger monoxides adopting the rocksalt structure at room conditions.[1] No indication of a transformation to the CsCl phase has been observed in this study. Upon decompression, the rocksalt structure in maintained beyond the upstroke transition pressure: ZnO reverts to the wurtzite structure at 1.9 ± 0.2 GPa, below which a single phase is present. The phase hysteresis is consequently substantial.

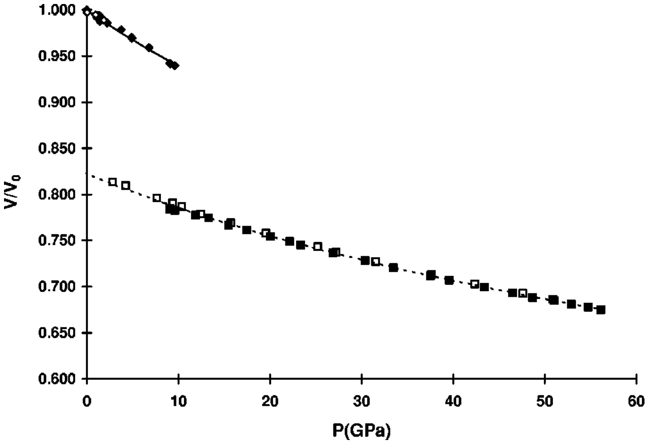

FIG. 2. Isothermal (300 K) equations of state of ZnO as measured by energy-dispersive x-ray diffraction. Solid and open symbols represent data points for increasing and decreasing pressures, respectively. Solid lines are Birch-Murnaghan equations of state plotted according to the compressive parameters given in Table I for each phase.

B. Structural and compressive parameters

Unit cell volumes were estimated based on at least eight diffraction lines throughout the pressure range covered, both in compression and decompression. The pressure dependence of the unit cell volume for both observed phases is given in Fig. 2. We have fitted, for each phase, all the compression and decompression data points to the third-order Birch-Murnaghan equation of state, known to give a realistic estimation of the compressive parameters, namely, the bulk modulus (B_0) and its pressure derivative (B_0') at null compression. For the wurtzite phase, when both B_0 and B_0' are varied during the χ^2 minimization, we obtain an unrealistically small B_0' and an increased B_0. For comparison with published results, we report a value of $B_0 = 142.7$ GPa which follows from a constraint of the value of B_0' to 3.6. For the rocksalt phase, we find an excellent convergence of the fit to the Birch-Murnaghan equation of state giving $B_0 = 202.5$ GPa, $B_0' = 3.54$, and $V/V_0 = 0.822$. The larger bulk modulus of the rocksalt phase is expected as it reflects the increase in oxygen coordination, from 4 to 6, as the structural transition proceeds from the wurtzite phase.

Compressive parameters for the wurtzite and the rocksalt phases of ZnO have been measured in the past by x-ray diffraction: values of bulk moduli and their associated pressure derivatives found in the literature cover a substantial range considering that both structures are relatively simple and thus their volumes are, in principle, easily evaluated. Present and published experimental results are presented in Table I. For the wurtzite phase, we find a substantial difference between the present results for B_0 and B_0' and those reported by Karzel *et al.*[4] and Gerward and Staun Olsen.[3] Whereas the former study gives a larger B_0 than what we have measured with a similar B_0', the latter reports a larger than usual value for the pressure derivative of the bulk modulus (9.4, in this case). On average, our measured B_0 and B_0' and the extrapolated volume at null compression for the rocksalt phase of ZnO (205.5 GPa, 3.54 and 19.6 Å^3) are in very good agreement with those of Bates, White, and Roy,

TABLE I. Structural and compressive parameters for the wurtzite and the rocksalt phases of ZnO. Subscript 0 refers to a parameter evaluated at null compression. Present and published data, both experimental and calculated, are presented. The bulk moduli and their associated pressure derivatives evaluated at room conditions are those obtained from χ^2 minimizations of the present data to the Birch-Murnaghan equation of state. Other experimental and calculated parameters are from the literature. Volumes are per chemical formula unit. The volume at null compression of the rocksalt structure was obtained from the fit. For the rocksalt phase, $P_{T\uparrow}$ and $P_{T\downarrow}$ indicate the transition pressures upon compression and decompression, respectively.

	Experimental				Calculated			
	Present data	Ref. 2	Ref. 4	Ref. 3	Ref. 5	Ref. 6	Ref. 4	Ref. 7
wurtzite								
$V_0(\text{Å}^3)$	23.810(6)		23.796	23.7847	24.570			
$a(\text{Å}),c(\text{Å})$	3.2498(3), 5.2066(3)		3.2496, 5.2042	4.2475, 5.2075	3.2903, 5.2414			
c/a	1.6021(3)		1.6018(7)	1.6035	1.593		1.604	
$d(c/a)/dP(GPa^{-1})$	$-0.0005(1)$		$-0.0007(3)$		-0.0005			
B_0 (GPa)	142.6(2)		183(7)	136(8)	154.4		160	
B_0'	3.6 (fixed)		4 (fixed)	9.4(15)	3.6		4.4	
rocksalt								
$V_0(\text{Å}^3)$	19.60(6)	19.60	19.484	19.60	19.799	18.8547		
$a_0(\text{Å})$	4.283(1)	4.28	4.271(2)	4.280(4)	4.2944	4.225		
B_0 (GPa)	202.5(2)	205.5	228(7)	170(10)	203.3	132	205	
B_0'	3.54(4)	3.6	4 (fixed)	9.5(9)	3.6	3.8	4.88	
$P_{T\uparrow}$ (GPa)	9.1(2)	9.5	8.7	$\simeq 10$	8.57		14.5	9.37
$P_{T\downarrow}$ (GPa)	1.9(2)		$\simeq 2$					

and Karzel *et al.*,[4] as given in Table I. We believe that the compressive parameters we report for the rocksalt phase of ZnO represent accurate values.

Calculated values of the compressive parameters of dense ZnO have been reported using different theoretical approaches: *ab initio* Hartree-Fock,[5] linear-augmented plane waves (LAPW),[4] *ab initio* perturbed-ion method,[6] and the extended ionic model.[7] Results are summarized in Table I. All calculations predict correctly the stability of the rocksalt structure as emerging from the wurtzite structure upon the application of pressure. A large range of values for the bulk moduli and their associated pressure derivatives of each phase and the wurtzite-rocksalt transition pressure have been reported. *Ab initio* weakly perturbed-ion calculations[6] give results of $B_0 = 132$ GPa and $B_0' = 3.8$, for the rocksalt phase, which are far what we have obtained. The latter approach which is based on the theory of separability of weakly overlapping groups have given good representations of total wave functions in a variety of systems and seems to give comparable results to those of the Hartree-Fock calculations as applied to the case of ZnS, but does not succeed equally as well to model dense ZnO. Calculations of Karzel *et al.*[4] (LAPW) yield substantially higher values of B_0 and B_0' (wurtzite: 160 GPa and 4.4; rocksalt: 205 GPa and 4.88) in comparison to what we have measured (wurtzite: 142.6 GPa and 3.6; rocksalt: 202.5 GPa and 3.54); the calculated parameters (LAPW) are, however, in closer agreement with their reported experimental results (wurtzite: 183 GPa and 4; rocksalt: 228 GPa and 4).

Our measured values of B_0 and B_0' are in very good agreement with those obtained from the Hartree-Fock calculation of Jaffe and Hess[5] (wurtzite: $B_0 = 154.4$ GPa and $B_0' = 4$; rocksalt: $B_0 = 203.3$ GPa and $B_0' = 4$), although the predicted transition pressure (8.57 GPa) is somewhat lower than actual observation (9.1 ± 0.2 GPa). It is also worth noting that we have found[14] a similar good agreement between the measured compressive parameters and those calculated using the Hartree-Fock method[15] for the case of dense ZnS, for which the wurtzite-rocksalt transition is also observed. Clearly, the Hartree-Fock method predicts, with a desired accuracy, total energy differences at different densities for a given phase or between phase of different phases in dense ZnO and, most likely, in other ionic/partially covalent solids.

C. Pressure dependence of the u parameter

The u parameter which describes the relative position of the anion sublattice with respect to the cation sublattice along the c axis in the wurtzite structure ($P6_3mc$, Zn at $\frac{1}{3},\frac{2}{3}$, 0 and $\frac{2}{3},\frac{1}{3},\frac{1}{2}$, and O at $\frac{1}{3},\frac{2}{3},u$, and $\frac{2}{3},\frac{1}{3},u+\frac{1}{2}$) is related to the c/a by $uc/a = (3/8)^{1/2}$. It has been assumed that the u parameter is closed to 3/8 for all compounds in the wurtzite structure. For ZnO and ZnS, Kisi and Elcombe[16] have in fact shown experimentally that there is a strict correlation between u and c/a, i.e., uc/a is near the ideal value $(3/8)^{1/2}$. The obvious questions which arise are whether the u parameter and the ideal correlation between u and c/a are affected by the compression of the ZnO wurtzite lattice.

We have measured a pressure change of the c/a axial ratio for the wurtzite phase of ZnO. Results are shown in Fig. 3. A linear relationship between the c/a and pressure is observed; a linear fit to the data gives $d(c/a)/dP = -0.0005 \pm 0.0001\ \text{GPa}^{-1}$, in very good agreement with published experimental[4] and calculated[5] values. Furthermore, we find no indication of an abnormal variation of the c/a near the structural transition pressure. If the ideal relationship between the axial ratio and the u positional parameter were to hold at higher density then an increase of u should be ex-

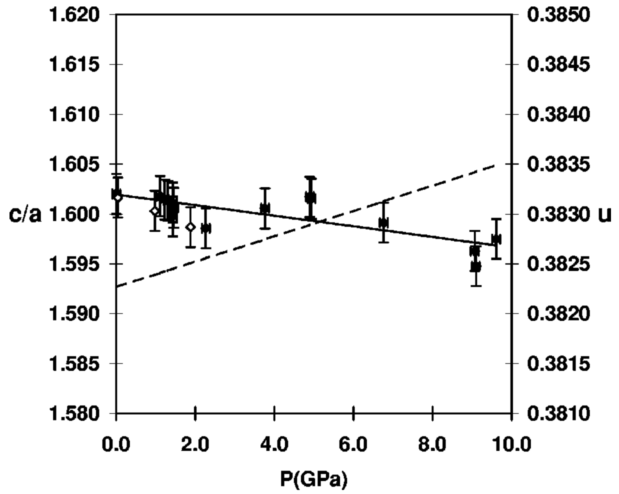

FIG. 3. Variation of the axial ratio of the wurtzite phase of ZnO under pressure at room temperature. A linear fit (solid line) gives a $c/a = 1.6021$ at room pressure and a pressure dependence of $-0.0005 \pm 0.0001\ \mathrm{GPa}^{-1}$. The broken line (right vertical scale) represents the pressure variation of the u oxygen positional parameter according to the ideal relationship $uc/a = (3/8)^{1/2}$.

pected accordingly, as shown in Fig. 3. In order to isolate the effect the pressure-induced change of the axial ratio on the u parameter versus a possible breakdown of the ideal relationship between the axial ratio and u, we have attempted to record, as a function of pressure, the variation of x-ray diffraction intensity consequent to the relative displacement of the anion sublattice with respect to that of the cation sublattice. For that purpose, we have evaluated at each pressure the integrated intensity of the wurtzite (002) and (101) x-ray diffraction lines, normalized to the recorded intensity of the Zn K_α fluorescence line to minimize the effect of the x-ray intensity and acquisition time. Our results indicate no obvious anomalies in the x-ray diffraction intensities which would lead to the conclusion that the u parameter deviates from its ideal value. It must be said, however, that we have recorded significant intensity fluctuations as a function of pressure as a result of poor x-ray diffraction intensity averaging due to a less-than-perfect powder and texture, as expected by using the energy-dispersive x-ray diffraction method. More work is underway to determine the accurate variation of the internal u parameter and its relationship with the axial ratio as a function of the external pressure on compounds adopting the wurtzite structure.

IV. CONCLUSION

Using energy-dispersive x-ray diffraction with synchrotron radiation at room temperature, we have observed, upon compression, the wurtzite-to-rocksalt transition at 9.1 ± 0.2 GPa in ZnO and established the rocksalt phase stability up to 56 ± 2 GPa. The compression parameters of the two phases are found to be, for the wurtzite and rocksalt phases, $B_0 = 142.6$ GPa and $B_0' = 3.6$ and $B_0 = 202.5$ GPa and $B_0' = 3.54$ with $V/V_0 = 0.822$, respectively. Our experimental results represent accurate equations of state data for dense ZnO and are in very good agreement with results obtained from Hartree-Fock calculations. Finally, we observe no indication that the u positional parameter deviates from the ideal $uc/a = (3/8)^{1/2}$ as wurtzite ZnO becomes denser.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the help of the entire CHESS staff and Dr. K. E. Brister. This work was financially supported by NSERC.

---

[1] L.-gun Liu and W. A. Bassett, *Elements, Oxides, and Silicates. High-Pressure Phases with Implications for the Earth's Interior* (Oxford University Press, New York, 1986).

[2] C. H. Bates, W. B. White, and R. Roy, Science **137**, 993 (1962).

[3] L. Gerward and J. Staun Olsen, J. Synchrotron Radiat. **2**, 233 (1995).

[4] H. Karzel, W. Potzel, M. Köferlein, W. Schiessl, U. Hiller, G. M. Kalvius, D. W. Mitchell, T. P. Das, P. Blaha, K. Schwarz, and M. P. Pasternak, Phys. Rev. B **53**, 11 425 (1996).

[5] J. E. Jaffe and A. C. Hess, Phys. Rev. B **48**, 7903 (1993).

[6] J. M. Recio, R. Pandey, and V. Luaña, Phys. Rev. B **47**, 3401 (1993).

[7] M. Wilson and P. A. Madden, Mol. Phys. **90**, 75 (1997).

[8] *High-velocity Impact Phenomena*, edited by R. Kinslow (Academic, New York, 1970).

[9] A. C. Mitchell and W. J. Nellis, J. Appl. Phys. **52**, 3363 (1981).

[10] W. J. Nellis, J. A. Moriarty, A. C. Mitchell, M. Ross, R. G. Dandrea, N. W. Ashcroft, N. C. Holmes, and G. R. Gathers, Phys. Rev. Lett. **60**, 1414 (1988).

[11] K. E. Brister, Y. K. Vohra, and A. L. Ruoff, Rev. Sci. Instrum. **57**, 2560 (1986).

[12] S. Desgreniers and K. Lagarec, J. Appl. Crystallogr. **27**, 432 (1994).

[13] S. Desgreniers and K. Lagarec, J. Appl. Crystallogr. **31**, 109 (1998); see also URL http://www.physics.uottawa.ca/~lpsd/xrda/xrda.htm

[14] S. Desgreniers and L. Beaulieu (unpublished).

[15] J. E. Jaffe, R. Pandey, and M. J. Seel, Phys. Rev. B **47**, 6299 (1993).

[16] E. Kisi and M. M. Elcombe, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **45**, 1867 (1989).