Rietveld refinement study of the pressure dependence of the internal structural parameter u in the wurtzite phase of ZnO

Haozhe Liu,[1,2] Yang Ding,[2] Maddury Somayazulu,[1,2] Jiang Qian,[3] Jinfu Shu,[2] Daniel Häusermann,[1,2] and Ho-kwang Mao[1,2]

[1]*HPCAT, Advanced Photon Source, Building 434E, Argonne National Laboratory, Argonne, Illinois 60439, USA*

[2]*Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA*

[3]*Lujan Neutron Scattering Center, Los Alamos National Laboratory, MS-H805, Los Alamos, New Mexico 87545, USA*

The pressure dependence of the internal structural parameter u of the wurtzite phase of ZnO was studied using high resolution angular dispersive x-ray diffraction up to 12 GPa in a helium pressure medium. The u parameter increases with pressure up to about 0.430 at about 5.6 GPa, and then rapidly decrease to about 0.380 during the phase transition. Two models of the phase transition path were proposed recently by first-principles calculations [A. M. Saitta and F. Decremps, Phys. Rev. B **70**, 035214 (2004); S. Limpijumnong and S. Jungthawan, Phys. Rev. B **70**, 054104 (2004)]. These possible mechanisms responsible for the wurtzite-to-rocksalt phase transition under high pressure are experimentally evaluated based on our results. The bulk moduli of the wurtzite and rocksalt phase at zero pressure were estimated as 135.3±1.8 and 177.4±4.6 GPa, respectively.

As one of the crystals analyzed by Bragg and Bragg using x-ray techniques,[1] ZnO has attracted a lot of attention over nearly a century from both experimental and theoretical points of view.[2–10] The pressure induced phase transition from wurtzite-to-rocksalt (B4-to-B1) structure was first reported by Bates *et al.* in 1962.[11] Synchrotron x-ray diffraction experiments on this phase transition were performed by various groups.[12–17] The mechanism responsible for this pressure induced phase transition, however, is not yet fully understood. Very recently, two separate groups reported the results of first-principles calculations on the possible path that would allow the least costly crossing of the transition enthalpy barrier.[18,19] From these calculations, the existences of possible metastable structures, i.e., an intermediate "tetragonal" phase, or "hexagonal" phase, were proposed, respectively. It is noticed that the internal structural parameter u [cf. the fractional atomic coordinates $(1/3, 2/3, u)$ for oxygen in $P6_3mc$ structure], which defines the relative position of the two sublattices in the hexagonal close-packed wurtzite structure, will show different pressure dependences depending on the transition path (see Fig. 1 in Ref. 18). Thus, high accuracy experimental measurement of $u(P)$ is needed to solve this puzzle, and to improve our understanding of the mechanism behind this common phase transition in semiconductors.

In situ high pressure angle-dispersive x-ray diffraction (ADXRD) experiments were carried out in a diamond anvil cell (DAC) apparatus at room temperature, and designed to generate hydrostatic conditions by using helium as a pressure medium.[20] Polycrystalline zinc monoxide with a nominal purity of 99.9995% (Puratronic®, Alfa Aesar) was prepressed to a pellet with thickness about 5 μm, and then loaded into the T301 stainless steel gasket sample hole which was about 45 μm in thickness at the start of the experiment. This guarantees that no sample bridging with anvils takes place during compression. One tiny ruby ball was loaded at the center of the sample chamber and the pressure was calibrated by the ruby luminescence method.[21] Time dependence of pressure in helium medium was monitored until equilibrium conditions were reached after each pressure change. The average of the pressure values which were measured before and after x-ray diffraction (XRD) patterns were taken are reported. The ADXRD experiments (λ=0.3888 Å) in a DAC were performed at beam line ID-B, HPCAT, Advanced Photon Source (APS), Argonne National Laboratory. A 400 μm x-ray beam was focused by K-B mirrors to about 15 μm (in diameter) at the sample position. Diffraction patterns were recorded on a MAR345 image plate with a typical exposure time of 60 s, and then integrated by using the program FIT2D.[22]

Representative high pressure XRD patterns are shown in Fig. 1 up to 15.5 GPa during the compression cycle. The wurtzite-to-rocksalt phase transition is observed in the range from 8.8 to 15.5 GPa. The corresponding Rietveld refinement for each pattern was carried out using GSAS package.[23] The refined internal structural parameter u in wurtzite phase is plotted in Fig. 2 as a function of pressure. In previous experimental studies, Desgreniers roughly estimated that the u values change under pressure by evaluating the integrated intensity of wurtzite (002) and (101) diffraction peaks from energy dispersive XRD (EDXRD) data.[13] As pointed out in his report, the accurate variation of the u parameter could not be determined due to the inherent disadvantage of EDXRD method in determining reliable intensities. Decremps *et al.* reported that the u value remained constant (within experimental errors) to 6.0 GPa,[16] then displayed a slight decrease with pressure based on the analysis of their high pressure extended x-ray-absorption fine-structure (EXAFS) data. This result, however, suffered from the technical difficulty to obtain high quality absorption signal through the diamond anvils under high pressure, and the well-known ambiguity that EXAFS analysis results are strongly dependent on the number of fitting parameters and the microstructural model used. The high pressure ^{67}Zn-Mössbauer spectroscopy measure-
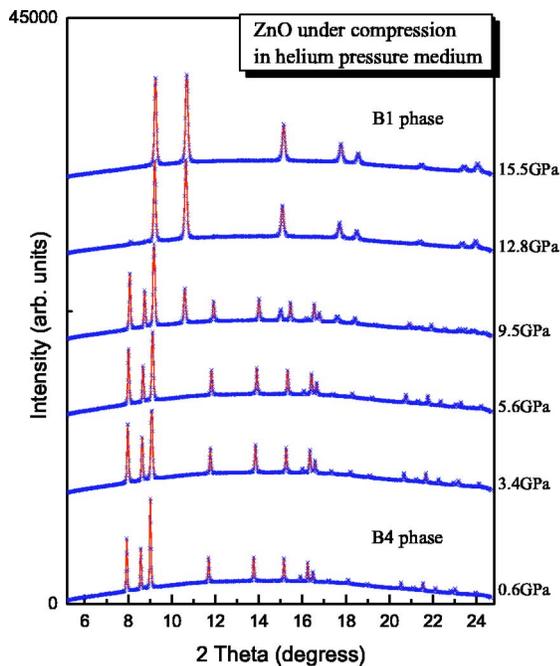
FIG. 1. (Color online) The typical ADXRD patterns of ZnO under high pressure.
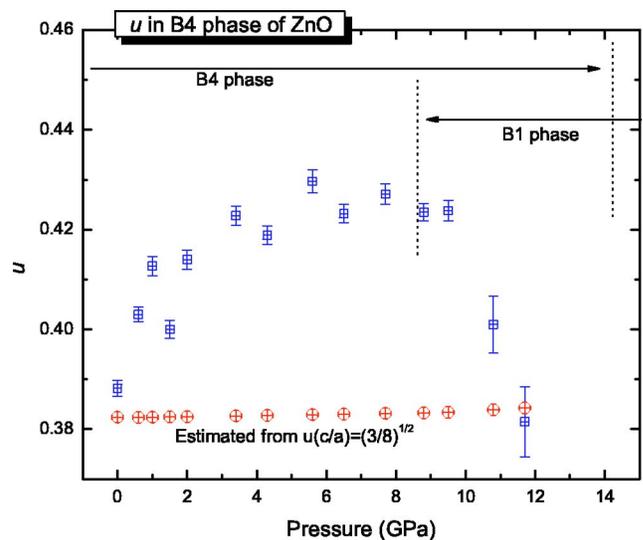

FIG. 2. (Color online) The internal structural parameter u of wurtzite structure ZnO as a function of pressure, in which Rietveld refinement: square symbol; and estimated from c/a ratio: circle symbol.

ment and Hartree-Fock and linearized-augmented plane-wave calculations studies for ZnO,[9] on the other hand, implied that the u value should increase with pressure.

In this paper, we show that Rietveld refinement of high resolution ADXRD data provides a more straightforward and precise information of the variation of u with pressure than previous estimates. From Fig. 2, it is clear that the u value increases with pressure up to about 0.430 at around 5.6 GPa. Thereafter, this trend changes and u slightly decreases with the increasing pressure, then drops quickly during the B4-to-B1 phase transition. Concomitantly, the c/a ratio decreases slightly with pressure from 1.601 to 1.593. It is noticed that the ideal correlation $uc/a=(3/8)^{1/2}$ between c/a ratio and u, which was experimentally confirmed by the wurtzite structural refinements of ZnO and ZnS at ambient conditions,[4] loses its validity under compression due to the large distortion of the wurtzite sublattice under pressure. The u values estimated from such an ideal correlation show slight increase with pressure as shown in Fig. 2.

These results shed light on the evaluation of the proposed phase transformation models. In the model suggested by Saitta and Decremps,[18] a distortion from wurtzite structure via a tetragonal path, wherein each Zn (or O) atom is located at the body center of square pyramid formed by five O (or Zn) atoms, while the c/a and u remain close to that of the B4 structure. In the next step, the c/a decreases to bring the Zn atom from the body center to the base center of the pyramid until $u=0.5$, resulting in the B1 structure. However, in an alternate model proposed by Limpijumnong and Jungthawan,[19] a different distortion, i.e., homogeneous B4-to-B1 phase transition could continuously follow the hexagonal path, in which the c/a ratio should decrease to about 1.22, and u increases from about 0.38 to 0.5. In spite of the fact that the c/a ratio shows a slight decrease with pressure,

the $u(P)$ trend in our experimental results show that the initial intermediate distortion path prefers the hexagonal model than the tetragonal model up to 5.6 GPa. However, the hexagonal intermediate path is not the ideal one used in calculations.[19] Therefore, any change of the c/a ratio would counter the variation of u under pressure. The u values quickly decrease during phase transition pressure range may imply that this distortion hexagonal intermediate phase is in competition with the alternative path.

The predicted B4 structure via the metastable hexagonal phase has never been observed experimentally, but could be calculated using the currently well developed first-principles simulations. For example, total energy calculations for B4 structure versus c/a ratio showed that the u value jumps to 0.5 above 24 GPa which is higher than the observed first order B4-to-B1 transition.[16] Thus, a suggestion to find this transformation at low temperature and high pressures remains to be investigated.[16] The B4 phase may remain stable to higher pressure range at low temperature compared to room temperature in spite of the fact that the slope of the phase boundary between B4 and B1 phase (dP/dT) is close to zero as estimated from the high temperature and high pressure experimental results.[15] The corresponding experiment at low T and high P is still worthy to be performed in the future to understand the B4-to-B1 phase transition mechanism by freezing this metastable phase from more general point of view.[24,25]

During the decompression process, some previous experiments showed that this B4-to-B1 phase transition reverted to B4 phase with pronounced hysteresis and this was a fully reversible transition.[9,13,16] However, other previous experiments found that the partially quenched B1 phase was retained with the B4 phase at ambient conditions.[11,12,14] In this study, the diffraction peaks of B4 phase appear at about 3.2 GPa in the decompression process, and then its fraction quickly increases in the two coexisting phases with decreas-

TABLE I. Equation of state parameters for ZnO at room temperature (XRD: x-ray diffraction, ADXRD: angle dispersive XRD, EDXRD: energy dispersive XRD, EXAFS: extended x-ray-absorption fine-structure, DAC: diamond anvil cell, LVA: large volume apparatus). The pressure range, pressure marker, and pressure medium in some previous reports were not clearly identified in text, and estimated from figures or experimental descriptions (marked by [*] in the table).

Structural type	B_0(GPa)	B'_0	Pressure range (GPa)	Pressure marker	Pressure medium	Techniques	Reference
B4	135.3±1.8	4 (fixed)	0–11.7	Ruby	Helium	ADXRD/DAC	This work run No. 1
	139.6±4.9	4 (fixed)	0–9.3	Ruby	Silicone oil	ADXRD/DAC	This work run No. 2
	183±7	4 (fixed)	0–15[*]	NaCl	NaCl	(Lab)XRD/DAC	9
	136±8	9.4(1)	0–10[*]	Ruby	Methanol/ethanol	EDXRD/DAC	12
	142.6±0.2	3.6 (fixed)	0–10	Cu	Silicone oil	EDXRD/DAC	13
	173	4 (fixed)	0–8.2	Ruby	Silicone oil	EDXRD/DAC	16
	181	4 (fixed)	0–9.1	Ruby	Silicone oil	EXAFS/DAC	16
	140±2	4 (fixed)	0–9[*]	Ruby	Methanol/ethanol/water	ADXRD/DAC	17
B1	177.7±4.6	4 (fixed)	8.8–15.5	Ruby	Helium	ADXRD/DAC	This work run No. 1
	194±11	4 (fixed)	11.1–29.3	Ruby	Silicone oil	ADXRD/DAC	This work run No. 2
	228±7	4 (fixed)	10.5–22.5[*]	Ruby	NaCl	(Lab)ADXR D/DAC	9
	170±10	9.5(9)	0–29[*]	Ruby	Methanol/ethanol	EDXRD/DAC	12
	202.5±0.2	3.54(4)	9.1–56[*]	Cu	Silicone oil	EDXRD/DAC	13
	194	4.8	0–30	Ruby	Methanol/ethanol	EDXRD/DAC	14
	191-201	3.54 (fixed)	2–11	NaCl	NaCl/BN	EDXRD/LVA	15
	204	4 (fixed)	2–15	Ruby	Silicone oil	EDXRD/DAC	16
	218	4 (fixed)	2–14	Ruby	Silicone oil	EXAFS/DAC	16
	194±20	4 (fixed)	9–202[*]	Au[*]	No medium[*]	ADXRD/DAC	17

ing pressure. It is interesting to notice that the very weak diffraction peak (200) of B1 phase still can be observed when pressure is released, and this weak peak coexists with B4 phase of ZnO for at least 2 days at ambient conditions. Apart from the catalyst effect, compression and heating history effects, the particle size effect of ZnO, for example, down to nanoscale, would significantly influence the phase stability pressure range, and the final fraction of B1 and B4 phase at ambient conditions.[26] The nanoscale grain size of ZnO did help in fully trapping the B1 phase at room conditions from the previous reports.[27] Thus a plausible explanation proposed for the previous contradictory reports is a little amount of B1 phase could be trapped in nanoscale grain size during B4-to-B1 transition in compression and then B1-to-B4 transition during decompression, which resulted in the partial B1 phase may still be observed even after pressure is released.

The bulk moduli of B4 and B1 phase were estimated by fitting the *P-V* data to a second order Birch equation of state.[28] The B_0 at zero pressure was estimated as 135.3±1.8 (B4 phase) and 177.4±4.6 GPa (B1 phase), respectively. Table I summaries the corresponding bulk moduli of B4 and B1 phase reported by previous studies. It is noticed that our data demonstrates relatively smaller bulk moduli than most of previous reports in which different pressure media were used. Thus separate experiments using silicone oil as pres-

sure medium were also performed, and larger bulk moduli were obtained. This is common behavior that hydrostatic pressure conditions yield more meaningful bulk modulus while the quasihydrostatic or nonhydrostatic conditions have a trend of overestimation of B_0.[29] The bulk moduli derived from our helium medium measurement provide more reliable B_0 values for the future first-principles calculations.

In summary, the pressure dependence of structural parameter *u* of wurtzite phase ZnO in helium pressure medium at room temperature was studied by Rietveld refinement of high resolution angular dispersive x-ray diffraction. The values of *u* increase with pressure, up to about 0.430 at around 5.6 GPa, and then rapidly decrease to about 0.380 during the phase transition process. This trend of distortion by hydrostatic pressure with pretransitional effect demonstrates that the initial intermediate distortion path prefers the hexagonal model. These structural evolutions under pressure derived from Rietveld refinement provide experimental confirmation to the corresponding first-principles simulations.

[1] W. H. Bragg and W. L. Bragg, *X-Rays and Crystal Structure* (Bell, London, 1915).

[2] S. C. Abrahams and J. L. Bernstein, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **25**, 1233 (1969).

[3] J. Albertsson and S. C. Abrahams, Acta Crystallogr., Sect. B: Struct. Sci. **45**, 34 (1989).

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

[5] J. E. Jaffe, R. Pandey, and A. B. Kunz, Phys. Rev. B **43**, 14030 (1991).

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

[7] J. Serrano, A. H. Romero, F. J. Manjón, R. Lauck, M. Cardona, and A. Rubio, Phys. Rev. B **69**, 094306 (2004).

[8] F. J. Manjón, K. Syassen, and R. Lauck, High Press. Res. **22**, 299 (2002).

[9] H. Karzel, W. Potzel, M. Köfferlein, W. Schiessl, M. Steiner, U. Hiller, G. M. Kalvius, D. W. Mitchell, T. P. Das, P. Blaha, K. Schwarz, and M. P. Pasternak, Phys. Rev. B **53**, 11425 (1996).

[10] J. E. Jaffe, J. A. Snyder, Z. Lin, and A. C. Hess, Phys. Rev. B **62**, 1660 (2000).

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

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

[13] S. Desgreniers, Phys. Rev. B **58**, 14102 (1998).

[14] J. M. Recio, M. A. Blanco, V. Luaňa, R. Pandey, L. Gerward, and J. S. Olsen, Phys. Rev. B **58**, 8949 (1998).

[15] F. Decremps, J. Zhang, and R. C. Liebermann, Europhys. Lett. **51**, 268 (2000).

[16] F. Decremps, F. Datchi, A. M. Saitta, A. Polian, S. Pascarelli, A. Di Cicco, J. P. Itié, and F. Baudelet, Phys. Rev. B **68**, 104101 (2003).

[17] Y. Mori, N. Niiya, K. Ukegawa, T. Mizuno, K. Takarabe, and A. L. Ruoff, Phys. Status Solidi B **241**, 3198 (2004).

[18] A. M. Saitta and F. Decremps, Phys. Rev. B **70**, 035214 (2004).

[19] S. Limpijumnong and S. Jungthawan, Phys. Rev. B **70**, 054104 (2004). To characterize the hexagonal-symmetry-breaking in-plane strain, two additional parameters were introduced to form a side-center orthorhombic structure for the B4 phase during the calculations.

[20] K. Takemura, J. Appl. Phys. **89**, 662 (2001).

[21] H. K. Mao, J. Xu, and P. M. Bell, J. Geophys. Res. **91**, 4673 (1986).

[22] A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch, and D. Häusermann, High Press. Res. **14**, 235 (1996).

[23] A. C. Larson, R. B. Von Dreele, General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR, 86-748 (1994).

[24] S. Limpijumnong and W. R. L. Lambrecht, Phys. Rev. Lett. **86**, 91 (2001).

[25] L. Bellaiche, K. Kunc, and J. M. Besson, Phys. Rev. B **54**, 8945 (1996).

[26] J. Z. Jiang, J. S. Olsen, L. Gerward, D. Frost, D. Rubie, and J. Peyronneau, Europhys. Lett. **50**, 48 (2000).

[27] F. Decremps, J. Pellicer-Porres, F. Datchi, J. P. Itié, A. Polian, F. Baudelet, and J. Z. Jiang, Appl. Phys. Lett. **81**, 4820 (2002).

[28] F. Birch, J. Geophys. Res. **83**, 1257 (1978).

[29] H. Liu, J. Hu, J. Shu, D. Häusermann, and H. K. Mao, Appl. Phys. Lett. **85**, 1973 (2004).