

## The High-Pressure Phase of Zincite

L. Gerward<sup>a</sup> and J. Staun Olsen<sup>b</sup>

<sup>a</sup>Physics Department, Technical University of Denmark, Building 307, DK-2800 Lyngby, Denmark, and <sup>b</sup>Niels Bohr Institute, Oersted Laboratory, University of Copenhagen, DK-2100 Copenhagen, Denmark

(Received 20 June 1995; accepted 11 July 1995)

Synchrotron-radiation X-ray diffraction studies of ZnO have been performed with special emphasis on the rock-salt-type high-pressure phase. The wurtzite (B4) to rock salt (B1) phase transformation is accompanied by a volume collapse of 18%, which is a very large effect. The lattice constant of the B1 phase at ambient pressure is  $a_0 = 4.280(4)$  Å, and the bulk modulus is  $B_0 = 170(10)$  GPa. Comparisons are made with a recently published theoretical equation of state obtained from *ab initio* perturbed-ion calculations.

**Keywords:** high-pressure phases; phase transformations; energy-dispersive powder diffraction; equation of state; zincite.

### 1. Introduction

The IIB–VIA binary compound semiconductors are an important group of technological materials. Most of them crystallize in the cubic zincblende or the hexagonal wurtzite-type structure. Their tetrahedral coordination is typical of  $sp^3$  covalent bonding. However, these materials also have a substantial ionic character (Phillips, 1970), and they tend to transform to the cubic rock-salt (NaCl) type structure by the application of high pressure. In most cases the high-pressure phase has been found to be metastable at lower pressure. Metastable rock-salt structure IIB–VIA compounds are expected to be interesting because of their unusual transport properties and optical properties (Jaffe, Pandey & Kunz, 1991).

The ambient form of ZnO is in the hexagonal wurtzite structure (B4). Bates, White & Roy (1962) discovered that a rock-salt-type (B1) phase could be quenched from pressures in the 10 GPa (100 kbar) range. Jamieson (1970), on the other hand, found the B4–B1 transition to be reversible at room temperature using *in situ* X-ray diffraction. A quantum-mechanical modelling of the high-pressure equation of state has recently been performed by Recio, Pandey & Luaña (1993) using an *ab initio* perturbed-ion (PI) approach. However, the equation of state in this phase has not been investigated experimentally as yet. The present work is a room temperature study of the polymorphism of zincite using synchrotron radiation and a diamond-anvil cell with special emphasis on the rock-salt-type high-pressure phase.

### 2. Experimental

X-ray powder diffraction spectra were recorded using synchrotron radiation and the white-beam energy-dispersive

method. High pressures were obtained in a diamond-anvil cell, where the powdered sample and a small ruby chip were enclosed in a hole of diameter 0.1 mm in an Inconel gasket. A 4:1 methanol/ethanol mixture was used as the pressure transmitting medium. The incident beam cross section was defined by a 0.1 mm pinhole slit or by two pairs of cross slits of 60 µm width. The pressure was determined from the wavelength shift of the ruby-line using the non-linear pressure scale of Mao, Bell, Shaner & Steinberg (1978). The Bragg angle associated with each series of diffraction spectra was found from a zero-pressure spectrum, where the sample in the diamond-anvil cell had been replaced by powdered NaCl with a known lattice constant.

The diffraction data were obtained at the high-energy beamline (station 9.7) of the UK Synchrotron Radiation Source (SRS) at Daresbury Laboratory using the energy-dispersive powder diffraction facility described by Clark (1992). This station receives radiation from a 5 T superconducting wiggler magnet with a useful photon flux from 5 to 60 keV. The diffraction spectra were recorded using a high-purity germanium detector and the Canberra S100 System. Another series of experiments were performed at HASYLAB-DESY in Hamburg, Germany, using the diffractometer described by Olsen (1992). The electron energy of the storage ring DORIS III was 3.7 GeV giving a useful photon energy range from 10 to 70 keV from a bending magnet. All experiments were made at room temperature.

The ZnO sample is one of a set of five oxide powders which are intended for use as standards for quantitative X-ray diffraction analysis. The particle-size distribution is centred about the 1 µm range. This standard reference material was obtained from the National Institute of Standards and Technology (NIST), Gaithersburg, Maryland, USA.

### 3. Results and discussion

#### 3.1. General observations

Fig. 1 shows the measured lattice-plane spacings as functions of pressure. A structural phase transformation is observed with a transition pressure  $P_{tr} \approx 10$  GPa, where the diffraction lines of the high-pressure f.c.c. phase begin to appear. The transition is completed at *ca* 15 GPa. The transition pressure is in good agreement with the experimental value of 9.5 GPa tabulated by Phillips (1971). The volume per formula unit can be calculated from the refined unit-cell parameters. The pressure–volume data obtained in this way (Fig. 2) have subsequently been fitted to the Birch (1938, 1947) equation of state:

$$P/B_0 = 3/2(x^{7/3} - x^{5/3})[1 + 3/4(B_0' - 4)(x^{2/3} - 1)]$$

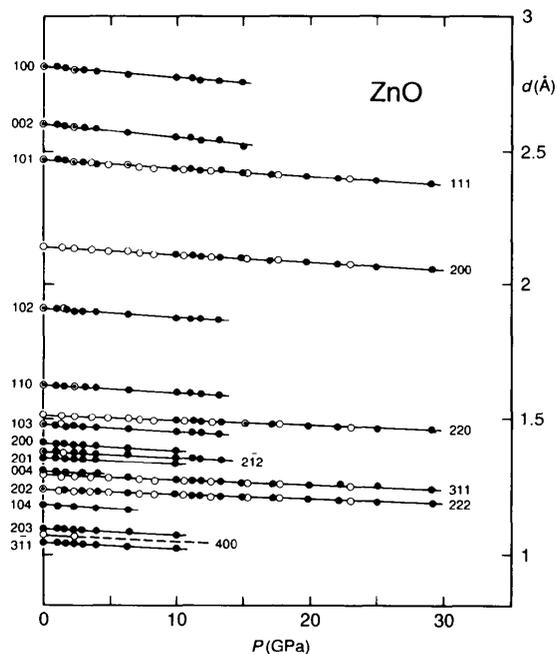
where  $x = V_0/V$ ,  $V_0$  being the volume at zero pressure and  $V$  the volume at pressure  $P$ . Here  $B_0$  is the isothermal bulk modulus and  $B_0'$  its pressure derivative, both evaluated at zero pressure. The parameters  $B_0$  and  $B_0'$  are refined by a least-squares method.

#### 3.2. The hexagonal wurtzite structure (B4)

Under normal conditions, zincite (ZnO) crystallizes in the hexagonal wurtzite (ZnS) type structure (B4), with space group  $P6_3mc$  (186). The unit cell contains  $Z = 2$  formula units. From a zero-pressure spectrum we obtain the lattice constants

$$a_0 = 3.2475 (6), c_0 = 5.2075 (20) \text{ \AA},$$

giving a calculated density  $\rho_0 = 5.682 (3) \text{ g cm}^{-3}$ . These



**Figure 1**

Lattice-plane spacings,  $d$ , as functions of pressure for ZnO. Filled symbols denote increasing pressure, and open symbols decreasing pressure. Miller indices  $hkl$  for the wurtzite phase (B4) are given to the left, and those for the rock-salt phase (B1) to the right.

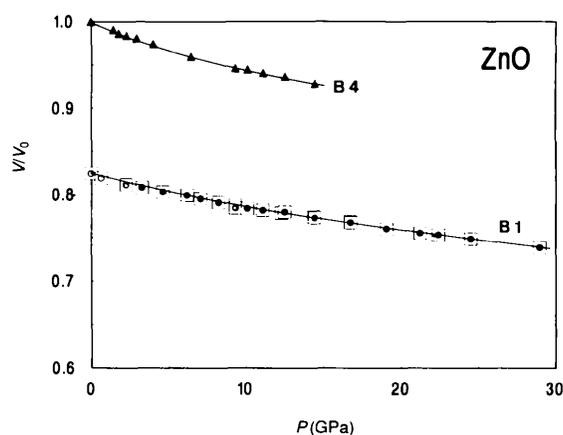
values are in good agreement with the NIST certified values 3.2491 (1) and 5.2065 (1) Å, respectively, and with the values 3.2498 (1) and 5.2066 (2) Å published by McMurdie *et al.* (1986). For the bulk modulus and its pressure derivative we obtain

$$B_0 = 136 (8) \text{ GPa}, B_0' = 9.4 (15),$$

where the uncertainties given in parentheses are the standard errors of the fit. The value of the bulk modulus is in good agreement with 144 GPa obtained by Bateman (1962) using an ultrasonic pulse technique. The equation of state of the B4 phase is shown in graphical form in Fig. 2.

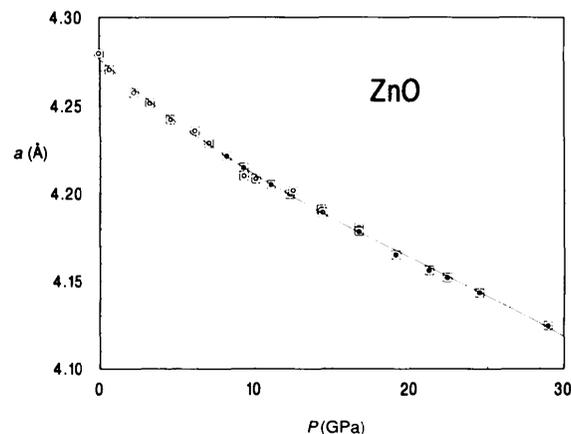
#### 3.3. The high-pressure rock-salt structure (B1)

It follows from Fig. 1 that a large fraction of the B1 high-pressure phase is retained when the pressure is released. Thus, it has also been possible to determine the equation of state for the rock-salt structure phase of ZnO. In Figs. 2 and 3 we show the pressure dependence of the relative volume



**Figure 2**

The equation of state for ZnO. The full curves have been calculated from the Birch equation. The upper curve is for the wurtzite phase (B4) and the lower curve for the rock-salt phase (B1).



**Figure 3**

The lattice constant of the rock-salt phase (B1) of ZnO as a function of pressure.

and the lattice constant, respectively. The lattice constant at atmospheric pressure is

$$a_0(\text{B1}) = 4.280(4) \text{ \AA},$$

in perfect agreement with the value quoted by Bates *et al.* (1962). The calculated density is  $\rho_0(\text{B1}) = 6.895(20) \text{ g cm}^{-3}$ . By comparison with the corresponding density of the B4 phase given above, it is seen that the B4 to B1 transition is accompanied by a volume collapse of 18%. This is a very large effect. In comparison, it may be mentioned that the well known B1–B2 transition in the alkali halides and other rock-salt structure compounds is generally associated with a volume change of *ca* 9%. For the bulk modulus and its pressure derivative we obtain from the Birch equation

$$B_0 = 170(10) \text{ GPa}, B_0' = 9.5(9).$$

To the best knowledge of the authors, there are no other experimental data with which to compare the present result. Usually, values of the pressure derivative  $B_0'$  should be close to 4. The rather large values found in the present work might, at least partially, be due to experimental problems. Owing to the large volume difference between B1- and B4-type ZnO, we had difficulties in measuring the pressure in the transition range, where the two phases are coexisting.

Table 1 summarizes selected results from the present work together with a comparison with the theoretical perturbed-ion calculations by Recio *et al.* (1993). There is a disagreement between theory and experiment with respect to the absolute values of the lattice constant. However, better agreement is obtained by considering the relative values  $a/a_0$ , where  $a$  is the lattice constant at pressure  $P$ , and  $a_0$  is the zero-pressure lattice constant. Our experiments give 0.984(2) at 10 GPa whereas the calculated value is 0.978. The theoretical value of the bulk modulus is *ca* 25% lower than the experimental value. It is to be noted, however, that the theoretical procedures reported for the rock-salt phase of ZnO in the meantime are being improved from a methodological point of view. It is expected that new calculations should give improved agreement with experiment (Recio, 1994).

**Table 1**

Lattice parameter and elastic constants of the rock-salt phase of ZnO.

$P$ (GPa)	$a$ (Å)	$B_0$ (GPa)	$B_0'$	Reference
0	4.280 (4)	170 (10)	9.5 (9)	This work
	4.225	132	3.8	PI calculation*
10	4.211 (3)			This work
	4.131			PI calculation*

\* Perturbed-ion calculation (Recio, Pandey & Luaña, 1993).

In conclusion, high-pressure X-ray diffraction experiments have confirmed the transition pressure and the zero-pressure lattice constant of rock-salt structure ZnO. The equation of state is in fair agreement with recent theoretical calculations. The B4–B1 transition is accompanied by an unusually large volume change of *ca* 18%.

We thank Daresbury Laboratory for use of the SRS under the EU Large-Scale Facilities Programme, and HASYLAB-DESY for permission to use the synchrotron radiation facility. Financial support from the Danish Natural Science Research Council is gratefully acknowledged.

## References

- Bateman, T. H. (1962). *J. Appl. Phys.* **33**, 3309–3312.  
 Bates, C. H., White, W. B. & Roy, R. (1962). *Science*, **137**, 993.  
 Birch, F. (1938). *J. Appl. Phys.* **9**, 279–288.  
 Birch, F. (1947). *Phys. Rev.* **71**, 809–824.  
 Clark, S. M. (1992). *Rev. Sci. Instrum.* **63**, 1010–1012.  
 Jaffe, J. E., Pandey, R. & Kunz, A. B. (1991). *Phys. Rev. B*, **43**, 14030–14034.  
 Jamieson, J. C. (1970). *Phys. Earth Planet. Inter.* **3**, 201–203.  
 McMurdie, H. F., Morris, M. C., Evans, E. H., Paretzkin, B., Wong-Ng, W. & Ettliger, L. (1986). *Powder Diffr.* **1**, 64–77.  
 Mao, H. K., Bell, P. M., Shaner, J. W. & Steinberg, D. J. (1978). *J. Appl. Phys.* **49**, 3276–3282.  
 Olsen, J. S. (1992). *Rev. Sci. Instrum.* **63**, 1058–1061.  
 Phillips, J. C. (1970). *Rev. Mod. Phys.* **42**, 317–356.  
 Phillips, J. C. (1971). *Phys. Rev. Lett.* **27**, 1197–1200.  
 Recio, J. M. (1994). Private communication.  
 Recio, J. M., Pandey, R. & Luaña, V. (1993). *Phys. Rev. B*, **47**, 3401–3403.