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High-pressure powder x-ray diffraction experiments on Zn at low temperature

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Abstract

High-pressure powder x-ray diffraction experiments have been performed on Zn with a He-pressure medium at low temperature. When the sample was compressed in the He medium at low temperature, large nonhydrostaticity developed, yielding erroneous lattice parameters. On the other hand, when the pressure was changed at high temperatures, good hydrostaticity was maintained. No anomaly in the volume dependence of the c/a axial ratio has been found.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Zinc is an hcp metal with a large c/a axial ratio. The axial ratio decreases under high pressure, giving rise to qualitative changes in the band structure and the Fermi surface. Theoretical calculations suggest that thermodynamic quantities should show anomalous changes when the topology of the Fermi surface changes [1]. This electronic topological transition (ETT) and consequent anomaly in the high-pressure behaviour of Zn are the focus of considerable current debate.

Early x-ray diffraction experiments seemed to show an anomaly in the volume dependence of the c/a axial ratio at 9.1 GPa and at room temperature [2, 3]. However, later experiments under better hydrostatic conditions no longer supported the existence of the c/a anomaly [4]. Neutron inelastic scattering experiments [5] and Raman scattering experiments [6] do not show any anomaly under high pressure. These experimental results are in strong contrast with theoretical calculations, which suggest the existence of a c/a anomaly [7–11]. It should be noted that only the Mössbauer experiment performed at 4 K reported the anomaly at 6.6 GPa [12, 13]. Since the Mössbauer experiment was done at low temperature, while other experiments were at room temperature, it was suggested that the ETT would be smeared out at room temperature due to thermal broadening of electron states [4, 8]. In order to get direct experimental proof of the c/a anomaly, we have performed high-pressure low-temperature powder x-ray diffraction experiments on Zn with a He-pressure medium.

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2. Experiments

We used a diamond-anvil cell (DAC) made of Cu–Be alloy designed for low-temperature work. A membrane with He gas drove the DAC. One of the diamond anvils was mounted on a B_4C backing plate, which allowed collection of full Debye–Scherrer rings up to 35° in 2θ. A fine powder of Zn was pressed into a thin plate and put into a hole in a spring steel gasket. The He-pressure medium was loaded into the DAC at room temperature with a high-pressure gas loading system operating at a gas pressure of 180 MPa [14]. The DAC was cooled down to 40 K in a closed-cycle He cryostat. The sample temperature was monitored with a thermocouple (Au–Fe (0.07%)/chromel) attached to one of the diamond anvils. The temperature sometimes fluctuated by about ± 10 K. However, since the thermal expansion of Zn is relatively small below 100 K [15], the change in the lattice parameters due to the temperature change is negligible. Pressure was determined with the hydrostatic ruby pressure scale [16]. A ruby chip on the table surface of a diamond anvil served as a reference at low temperature. Angle-dispersive powder x-ray diffraction experiments were carried out on the bending magnet beamline 18C of the Photon Factory by using a monochromatic beam with an x-ray energy of 20.0 keV. The diffraction patterns were recorded on imaging plates [17] and were analysed with the pattern integration software 'pip' [18].

Helium is the best hydrostatic pressure medium [19], but it is known to develop nonhydrostaticity if compressed at low temperature [20]. In order to check the effect of nonhydrostaticity and reproducibility, we have made three experimental runs. In run A, pressure was changed at low temperature. In two other runs, B and C, pressure was changed at high temperature near the melting point of He at each pressure [21, 22].

3. Results and discussion

Figure 1 shows a representative powder x-ray diffraction pattern of Zn in run B at high pressure and low temperature. Diffraction peaks are sharp, indicating good hydrostaticity of the present experiments. Another indication of hydrostaticity is the presence of the 002 reflection. If the pressure is not hydrostatic, the 002 reflection is hardly observed due to the preferred orientation of the specimen [4]. The lattice parameters a and c were determined within $\pm 0.12\%$ by using 6–10 reflections.

Figure 2 shows the difference in lattice parameter a obtained in runs A, B, and C. If the sample is directly compressed at low temperature (run A), the measured lattice parameter is completely different from those for the other two runs. In addition, there is large hysteresis between increasing and decreasing pressure cycles. This can be explained by the effect of nonhydrostaticity. If the sample is compressed in solid He at low temperature, large uniaxial stress develops along the load axis. Under such conditions, lattice planes lying perpendicular to the load axis are much more compressed than in the hydrostatic case, while planes parallel to the load axis are relatively expanded [4, 19]. In the present diffraction geometry, the incident x-rays are parallel to the load axis, satisfying the Bragg condition only for the planes lying nearly parallel to the load axis. Consequently, the observed interplanar spacings and lattice parameters become larger than in the hydrostatic case. The lattice parameter c measured in run A was less affected by the nonhydrostaticity, but because of the apparent expansion of the a-axis, the c/a axial ratio obtained in run A was much smaller than those from runs B and C.

The results of runs B and C are consistent with each other. Figure 3 summarizes the variation with pressure of the lattice parameters and axial ratio at room and low temperatures. The lattice parameters connect smoothly with the values at atmospheric pressure at low temperature [23]. The variations of the lattice parameters and axial ratio show no anomaly

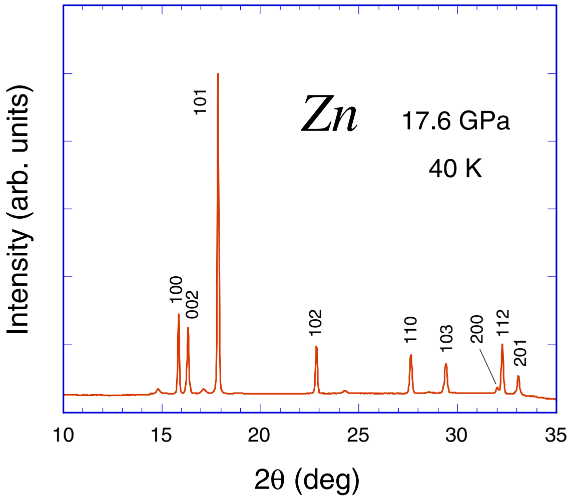

Figure 1. The powder x-ray diffraction pattern of Zn at 17.6 GPa and 40 K with a He-pressure medium. The x-ray energy was 20.0 keV. The weak unindexed peaks are associated with ZnO formed on the surface of the Zn specimen.

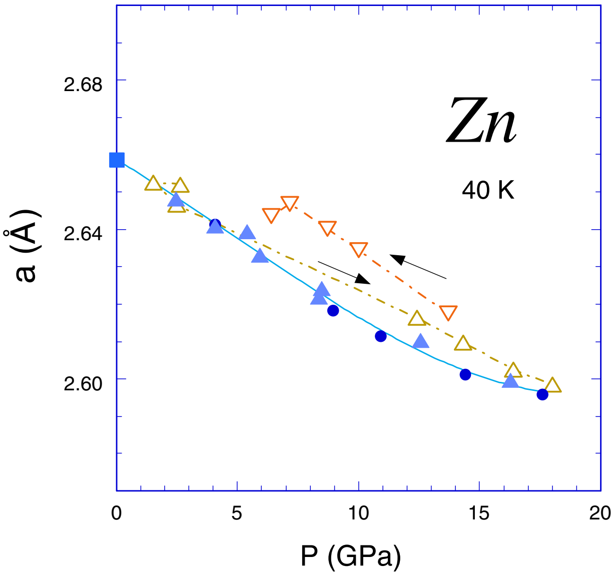

Figure 2. The lattice parameter *a* obtained in three different runs. In run A (open triangles), pressure was changed at low temperature. In runs B and C (closed circles and triangles), pressure was changed at high temperature. All the data were taken with the He-pressure medium. The square shows the value at atmospheric pressure [23].

and merge into the change at room temperature at high pressures. This means that the thermal expansion of Zn rapidly decreases at high pressures.

Figure 4 shows the variation of the axial ratio plotted as a function of relative volume V/V_0, where V_0 refers to the volume at atmospheric pressure and at 4 K [23]. Theoretical calculations are compared in the figure. Early calculations [7–9] show large anomalies in the

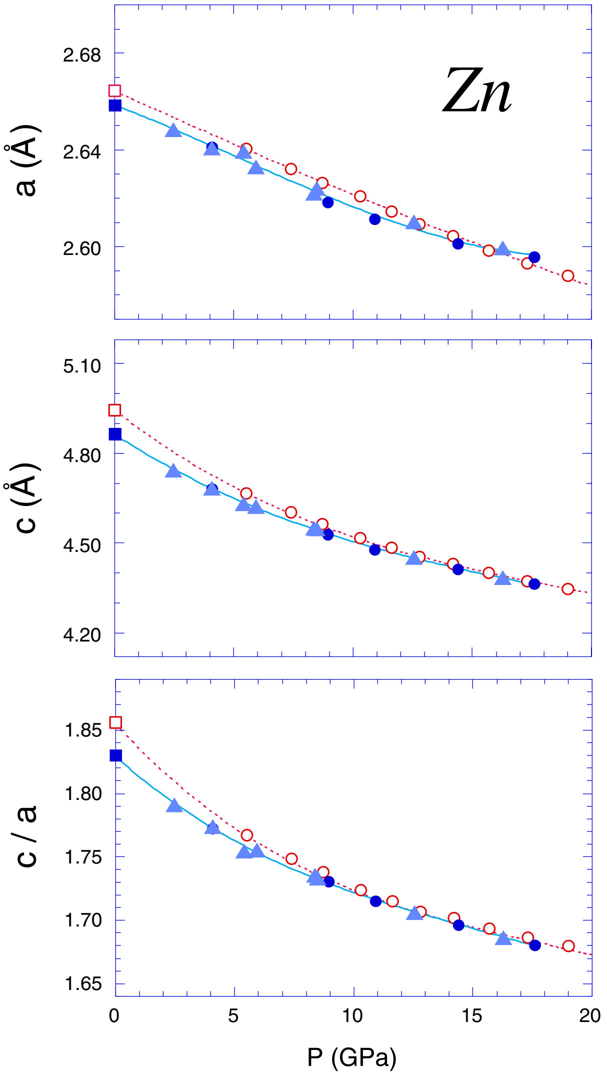

Figure 3. Lattice parameters and the axial ratio of Zn at high pressures. Closed symbols indicate the present experimental results obtained at 40 K, and open symbols those obtained at 297 K from [4]. Only the data taken in runs B and C are included. The squares show the data taken at atmospheric pressure [23, 24].

volume range $V/V_0 = 0.88$–0.90. By contrast, a recent calculation by Li and Tse [11] shows a very weak anomaly in the same volume range.

The calculation by Steinle-Neumann *et al* [25] indicates no anomaly at all. The present experimental data obviously disagree with the three early calculations. However, if the anomaly is as small as the calculation by Li and Tse indicates, it is difficult to detect within the present experimental uncertainty. In any case the present result provides an upper limit for the lattice anomaly, if it does exist.

In summary, the present experiments show that there is no detectable anomaly in the volume dependence of the axial ratio of Zn at low temperature. It is, however, possible that the lattice anomaly associated with the ETT is extremely small and beyond the current experimental

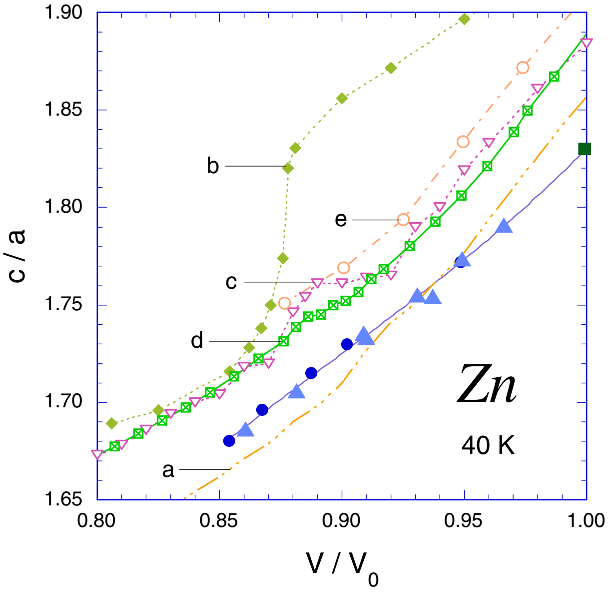

Figure 4. Variation of the c/a axial ratio of Zn at low temperatures as a function of relative volume V/V_0, where V_0 refers to the volume at atmospheric pressure and at 4 K [23]. The closed circles and triangles are the present experimental data obtained at 40 K with a He-pressure medium. The closed square indicates the value at atmospheric pressure and at 40 K [23]. The curves (a)–(e) are theoretical calculations: (a) [7]; (b) [8]; (c) [9]; (d) [11]; and (e) [25].

precision. The present work demonstrates that hydrostaticity is crucial to investigating delicate lattice properties especially at low temperature. Further experiments with various high-pressure techniques are encouraged in order to identify the ETT at low temperature.

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References

[1] Lifshitz I M 1960 *Zh. Eksp. Teor. Fiz.* **38** 1569 (Engl. transl. 1960 *Sov. Phys.–JETP* **11** 1130)
[2] Takemura K 1995 *Phys. Rev. Lett.* **75** 1807
[3] Takemura K 1997 *Phys. Rev.* B **56** 5170
[4] Takemura K 1999 *Phys. Rev.* B **60** 6171
[5] Klotz S, Braden M and Besson J M 1998 *Phys. Rev. Lett.* **81** 1239
[6] Olijnyk H, Jephcoat A P, Novikov D L and Christensen N E 2000 *Phys. Rev.* B **62** 5508
[7] Meenakshi S, Vijayakumar V, Godwal B K and Sikka S K 1992 *Phys. Rev.* B **46** 14 359
[8] Fast L, Ahuja R, Nordström L, Wills J M, Johansson B and Eriksson O 1997 *Phys. Rev. Lett.* **79** 2301
[9] Novikov D L, Freeman A J, Christensen N E, Svane A and Rodriguez C O 1997 *Phys. Rev.* B **56** 7206
[10] Novikov D L, Katsnelson M I, Trefilov A V, Freeman A J, Christensen N E, Svane A and Rodriguez C O 1999 *Phys. Rev.* B **59** 4557
[11] Li Zhiqiang and Tse J S 2000 *Phys. Rev. Lett.* **85** 5130
[12] Potzel W, Steiner M, Karzel H, Schiessl W, Köfferlein M, Kalvius G M and Blaha P 1995 *Phys. Rev. Lett.* **74** 1139

[13] Steiner M, Potzel W, Karzel H, Schiessl W, Köfferlein M, Kalvius G M and Blaha P 1996 *J. Phys.: Condens. Matter* **8** 3581

[14] Takemura K, Sahu P Ch, Kunii Y and Toma Y 2001 *Rev. Sci. Instrum.* **72** 3873

[15] McCammon R D and White G K 1965 *Phil. Mag.* **11** 1125

[16] Zha Chang-Sheng, Mao Ho-kwang and Hemley R J 2000 *Proc. Natl Acad. Sci. USA* **97** 13 494

[17] Shimomura O, Takemura K, Fujihisa H, Fujii Y, Ohishi Y, Kikegawa T, Amemiya Y and Matsushita T 1992 *Rev. Sci. Instrum.* **63** 967

[18] Fujihisa H, unpublished

[19] Takemura K 2001 *J. Appl. Phys.* **89** 662

[20] Reimann K 1996 *High Pressure Res.* **15** 73

[21] Vos W L, van Hinsberg M G E and Schouten J A 1990 *Phys. Rev.* B **42** 6106

[22] Datchi F, Loubeyre P and LeToullec R 2000 *Phys. Rev.* B **61** 6535

[23] The lattice parameters of Zn at low temperature and at atmospheric pressure were calculated by combining the data near room temperature:
Owen E A and Yates E L 1934 *Phil. Mag.* **17** 113
together with the thermal expansion data from [15].

[24] Donohue J 1974 *The Structures of the Elements* (New York: Wiley) p 225

[25] Steinle-Neumann G, Stixrude L and Cohen R E 2001 *Phys. Rev.* B **63** 054103