Axial ratio of Zn at high pressure and low temperature

Takemura Kenichi*

National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044, Japan

Yamawaki Hiroshi and Fujihisa Hiroshi

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan

Kikegawa Takumi

Photon Factory, Institute of Materials Structure Science, Tsukuba, Ibaraki 305-0801, Japan

High-pressure powder x-ray-diffraction experiments have been carried out on Zn with a He-pressure medium up to 18 GPa at 40 K. No anomaly in the volume dependence of the c/a axial ratio has been found within experimental errors. The c/a anomaly, which has been predicted to appear associated with the electronic topological transitions, should be extremely small. Thermal expansion of Zn rapidly decreases under high pressure, yielding nearly identical axial ratios at room and low temperatures.

Zinc is an anisotropic hcp metal. The c/a axial ratio is unusually large compared with normal hcp metals. The linear compressibility of the c axis is about eight times larger than that of the a axis. Consequently, the c/a axial ratio of Zn rapidly decreases under high pressure. The large variation of the axial ratio induces drastic changes in the band structure and the Fermi surface without accompanying structural phase transitions. In this respect, Zn is an interesting substance to study the correlation between crystal structure and electronic properties.

In 1995, Takemura carried out powder x-ray-diffraction experiments on Zn at room temperature.[1,2] He found an anomaly in the volume dependence of the c/a ratio at 9.1 GPa: the axial ratio vs V/V_0 curve changes the slope at this pressure. The anomaly was interpreted either as a singularity of the hcp structure or an electronic topological transition (ETT), which refers to a topological change of the Fermi surface. Shortly before the x-ray experiment, an anomaly was also found in the Mössbauer spectra of Zn at 6.6 GPa at low temperature.[3] The abrupt decrease of the Lamb-Mössbauer factor or the softening of the crystal lattice was attributed to the ETT. These two experiments stimulated subsequent theoretical investigations on Zn under high pressure. A number of calculations reproduced the anomaly in the c/a ratio and found the cause of the anomaly in the ETTs.[4–7] The interpretation seemed reasonable, since the density of states at the Fermi level suddenly changes at the ETTs and may cause lattice anomaly as Lifshitz justified.[8]

However, in later powder x-ray-diffraction experiments with a He-pressure medium, the c/a anomaly completely disappeared.[9] The c/a anomaly in the previous experiment was most probably produced by nonhydrostaticity of the alcohol-water pressure medium.[9] Inelastic neutron-scattering experiments on Zn showed no anomaly in the acoustic phonon frequency up to 9.4 GPa at room temperature.[10] Raman-scattering experiments showed no discontinuity in the optical phonon frequency up to 58 GPa at room temperature, although an indication of the ETT was suggested in the change

in the Raman peak width.[11] These experimental results indicate that there is no anomaly in the lattice dynamics of Zn under pressure at room temperature. New calculations followed the experiments. Li and Tse confirmed the c/a anomaly, although the magnitude of their anomaly is much smaller than other calculations.[12] Steinle-Neumann *et al.* pointed out that the c/a anomaly is very sensitive to the Brillouin-zone sampling, and should disappear if a sufficient number of k points is used for the calculation.[13] Kechin studied details of the ETTs at the K and L symmetry points of the Brillouin zone.[14]

So far, serious controversy exists about the existence of the c/a anomaly in theory and experiments. One of the possible explanations for the disagreement is the effect of temperature. The c/a anomaly, which may exist at low temperature, would smear out at room temperature due to thermal broadening of electron states.[5] This hypothesis explains why the Mössbauer experiments detected the anomaly at low temperature, while other experiments at room temperature did not. In order to prove whether the c/a anomaly actually exists at low temperature, we have carried out powder x-ray-diffraction experiments on Zn at low temperature. We used a He-pressure medium, which proved to be the best hydrostatic pressure medium.[15]

Powder x-ray-diffraction experiments at low temperature have been done with a diamond-anvil cell (DAC). The DAC was made of Cu-Be alloy and was pressurized by a membrane filled with He gas. The diamond anvil on the exit side of the x rays was mounted on a B_4C plate, which allowed collection of full Debye-Scherrer rings up to 35° in 2θ. Special care was taken not to pressurize the sample directly with the diamond anvils at high pressures. A fine powder of Zn (99% purity) was lightly pressed into a thin plate of 15 μm thickness. A small piece was cut from the plate and put into a hole in a spring steel gasket. The sample thickness was small enough compared with the final thickness of the gasket ($\sim$30 μm) at the highest pressure. The He-pressure me-

dium was loaded to the DAC at room temperature with a high-pressure gas loading system.[16]

Experiments have been done at 40 K in a He cryostat equipped with a closed-cycle refrigerator. Sample temperature was monitored with a Au-Fe (0.07%)/chromel thermocouple attached to one of the diamond anvils. The temperature fluctuated between 30 and 50 K. It should be noted, however, that the thermal expansion of Zn below 100 K is so small that the change in the lattice parameters due to the temperature change of ± 10 K is negligible.[17] Helium is known to develop nonhydrostaticity, if compressed at low temperature.[18] Therefore, pressure was changed at high temperature near the melting point of He at each pressure.[19,20] A microheater made of a manganin wire was placed around one of the diamond anvils and was used to raise the sample temperature quickly. It was also important to control the He gas pressure in the membrane so as to minimize unwanted pressure change during the cooling process of the DAC. Pressure was determined with the hydrostatic ruby pressure scale,[21] assuming that the pressure dependence of the ruby fluorescence at low temperature is the same as that at room temperature.[22] A ruby chip placed on the outer surface of a diamond anvil served as a reference at low temperature. Powder x-ray-diffraction experiments were carried out in the angle-dispersive mode on the bending magnet beam line 18C of the Photon Factory. The x ray was monochromatized to an energy of 20.0 keV. Diffraction patterns were recorded on imaging plates,[23] and were analyzed with the pattern integration software PIP.[24]

Two experimental runs gave consistent results.[25] Figure 1 shows representative powder x-ray-diffraction patterns of Zn at high pressures and low temperature. Diffraction peaks remain sharp up to the highest pressure, indicating good hydrostaticity of the present experiments. Another indication of hydrostaticity is the persistence of the (002) reflection. If the pressure is not hydrostatic, the (002) reflection is hardly observed due to the preferred orientation of the specimen.[9] The lattice parameters a and c were determined within $\pm 0.12\%$ from the peak positions of 6–10 reflections.

Figure 2 shows the variation of the lattice parameters with pressure at 297 K (Ref. 9) and 40 K. The results of the two experimental runs at low temperature are consistent as shown by closed circles and triangles. The present data smoothly connect with the values at atmospheric pressure and low temperature.[26] The variation of the lattice parameters at high pressures shows no anomaly. As a consequence, no anomaly is seen in the pressure-volume curve at low temperature. One notices that the difference of the lattice parameters at 297 K and 40 K decreases with pressure and approaches zero above about 15 GPa. It means that the thermal expansion of Zn rapidly decreases at high pressures. The thermal expansion of Zn at atmospheric pressure is fairly large compared with other hcp metals, reflecting large anharmonicity.[28] Pressure reduces the anharmonicity and makes Zn behave normally. The present data even suggest negative thermal expansion of the a axis above 16 GPa, but further experiments are necessary to confirm it. It is interesting to note that a change of sign of the thermal expansion was predicted by theory in the region of ETT.[7]
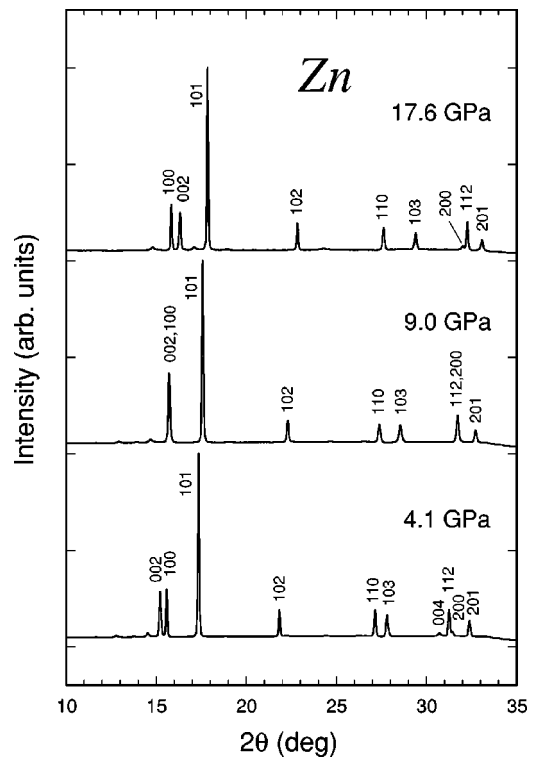

FIG. 1. Powder x-ray-diffraction patterns of Zn at 40 K with a He-pressure medium. The x-ray energy was 20.0 keV. Weak unindexed peaks are of ZnO formed on the surface of the Zn specimen. Note that the (002) reflection is clearly observed up to the highest pressure, indicating good hydrostaticity.

Figure 3 shows the variation of the axial ratio with pressure at 297 K and 40 K. The present low-temperature data smoothly connect with the value at atmospheric pressure.[26] The variation of the axial ratio in the low-pressure region is in good agreement with the estimation based on the elastic constants at low temperature.[29] Reflecting the rapid decease
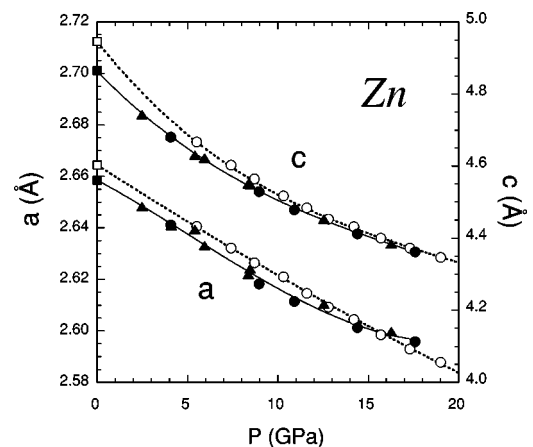

FIG. 2. Lattice parameters of Zn at 297 K (open circles) and at 40 K (closed circles and triangles) under high pressure. All the data were taken with the He-pressure medium. The data at 297 K are from the previous study (Ref. 9). The squares show the data at atmospheric pressure from the literature (Refs. 26 and 27). Note the different scale for the a and c axes.
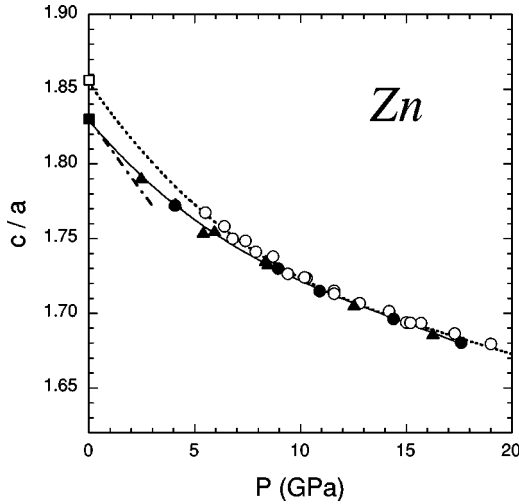
FIG. 3. Axial ratio of Zn at 297 K (open circles, Ref. 9) and 40 K (closed circles and triangles) under high pressure. The squares show the data at atmospheric pressure from the literature (Refs. 26 and 27). The dash-dotted curve shows the pressure dependence of the axial ratio at low temperature calculated from Ref. 29. The curves are a guide for the eye.

of the thermal expansion at high pressures, the axial ratio at low temperature converges to the ratio at room temperature above about 10 GPa. No anomaly is seen in the variation of the axial ratio.

Figure 4 shows the variation of the axial ratio as a function of relative volume V/V_0, where V_0 refers to the volume at atmospheric pressure and at 4 K.[26] Theoretical calculations a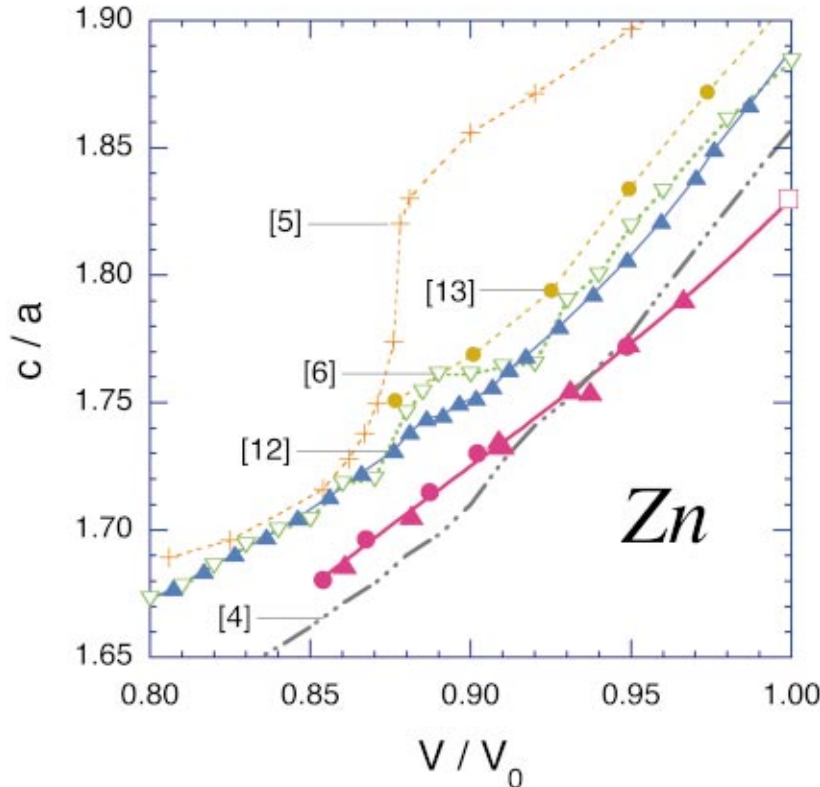re included in the figure for comparison. It should be noted that the calculated equilibrium volumes V_0 differ by calculations, because of the well-known insufficiency of the local-density approximation.[6] Early calculations[4–6] show large anomalies over the volume range $V/V_0=0.88$–0.90. The present experimental data obviously disagree with them. The recent calculations, on the other hand, show very weak anomaly,[12] or no anomaly[13] over the same volume range. If the anomaly is so small as, for example, the calculation by Li and Tse indicates,[12] it is beyond the present experimental uncertainty. In this respect the present result constrains the upper limit of the lattice anomaly. The anomaly, if it does exist, should be less than 0.35% or 0.006 in c/a. The present experiments also do not rule out the possibility that the anomaly may appear at pressures higher than 18 GPa at low temperature. Further experiments with various high-pressure techniques would be necessary to identify the ETT in Zn at low temperature.

In summary, the present study reveals that there is no detectable anomaly in the volume dependence of the axial ratio of Zn up to 18 GPa at low temperature. The thermal expansion of Zn rapidly decreases with pressure, leading to the nearly identical axial ratio at room and low temperatures above 10 GPa. The present work offers the upper limit for the c/a anomaly in Zn, if the ETT really induces lattice anomaly.

FIG. 4. (Color) Variation of the c/a axial ratio of Zn at low temperature as a function of relative volume V/V_0, where V_0 denotes the volume at atmospheric pressure and at 4 K. The red closed circles and triangles are the present experimental data obtained at 40 K with a He-pressure medium. The red open square indicates the value at atmospheric pressure and at 40 K (Ref. 26). The curves labeled with reference numbers represent theoretical calculations for 0 K.

*Electronic address: takemura.kenichi@nims.go.jp

[1] K. Takemura, Phys. Rev. Lett. **75**, 1807 (1995).

[2] K. Takemura, Phys. Rev. B **56**, 5170 (1997).

[3] W. Potzel, M. Steiner, H. Karzel, W. Schiessl, M. Köfferlein, G.M. Kalvius, and P. Blaha, Phys. Rev. Lett. **74**, 1139 (1995).

[4] S. Meenakshi, V. Vijayakumar, B.K. Godwal, and S.K. Sikka, Phys. Rev. B **46**, 14 359 (1992).

[5] L. Fast, R. Ahuja, L. Nordström, J.M. Wills, B. Johansson, and O. Eriksson, Phys. Rev. Lett. **79**, 2301 (1997).

[6] D.L. Novikov, A.J. Freeman, N.E. Christensen, A. Svane, and C.O. Rodriguez, Phys. Rev. B **56**, 7206 (1997).

[7] D.L. Novikov, M.I. Katsnelson, A.V. Trefilov, A.J. Freeman, N.E. Christensen, A. Svane, and C.O. Rodriguez, Phys. Rev. B **59**, 4557 (1999).

[8] I.M. Lifshitz, Zh. Éksp. Teor. Fiz. **38**, 1569 (1960) [Sov. Phys. JETP **11**, 1130 (1960)].

[9] K. Takemura, Phys. Rev. B **60**, 6171 (1999).

[10] S. Klotz, M. Braden, and J.M. Besson, Phys. Rev. Lett. **81**, 1239 (1998).

[11] H. Olijnyk, A.P. Jephcoat, D.L. Novikov, and N.E. Christensen, Phys. Rev. B **62**, 5508 (2000).

[12] Zhiqiang Li and J.S. Tse, Phys. Rev. Lett. **85**, 5130 (2000).

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

[14] V.V. Kechin, Phys. Rev. B **63**, 045119 (2001).

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

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

[17] R.D. McCammon and G.K. White, Philos. Mag. **11**, 1125 (1965).

[18] See, for example, K. Reimann, High Press. Res. **15**, 73 (1996).

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

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

[21] Chang-Sheng Zha, Ho-kwang Mao, and Russell J. Hemley, Proc. Natl. Acad. Sci. U.S.A. **97**, 13 494 (2000).

[22] K. Nakano, Y. Akahama, Y. Ohishi, and H. Kawamura, Jpn. J. Appl. Phys., Part 1 **39**, 1249 (2000).

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

[24] H. Fujihisa (unpublished).

[25] We have done one more experimental run, in which pressure was directly changed at low temperature. The obtained lattice parameters and axial ratio were completely different from the present results due to the presence of nonhydrostaticity. The detailed account of the effect of nonhydrostaticity at low temperature will be published elsewhere.

[26] The lattice parameters of Zn at low temperature and at atmospheric pressure were calculated by combining the data near room temperature [E.A. Owen and E.L. Yates, Philos. Mag. **17**, 113 (1934)] together with the thermal-expansion data from Ref. 17.

[27] J. Donohue, *The Structures of the Elements* (Wiley, New York, 1974), p. 225.

[28] K.A. Gschneidner, Jr., Solid State Phys. **16**, 275 (1964).

[29] G.A. Alers and J.R. Neighbours, J. Phys. Chem. Solids **7**, 58 (1958).