

PHYSICAL REVIEW B

CONDENSED MATTER AND MATERIALS PHYSICS

THIRD SERIES, VOLUME 60, NUMBER 9

1 SEPTEMBER 1999-I

BRIEF REPORTS

Brief Reports are accounts of completed research which, while meeting the usual Physical Review B standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.

Absence of the c/a anomaly in Zn under high pressure with a helium-pressure medium

Takemura Kenichi*

National Institute for Research in Inorganic Materials (NIRIM), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

(Received 8 April 1999)

A high-pressure powder x-ray diffraction experiment on Zn has been carried out at room temperature with He pressure-transmitting medium in order to achieve the best hydrostatic conditions. The anomaly in the volume-dependence of the c/a axial ratio, which has been observed previously, can no longer be observed. Hence the anomaly is most probably induced by the nonhydrostaticity associated with the solidification of the methanol-ethanol-water pressure-transmitting medium used in the previous studies. The present results suggest reconsideration of the calculated c/a anomaly based on the electronic topological transition.

[S0163-1829(99)11233-5]

Zinc has an unusually large c/a axial ratio (1.856) for the hcp structure under ambient conditions. The deviation of the axial ratio from the ideal value (1.633) has been explained by the reduction in the band-structure energy through lattice distortion.¹⁻⁴ The axial ratio of Zn decreases under high pressure and has been investigated recently with high precision.⁵ It reports an interesting phenomenon: the volume dependence of the c/a axial ratio changes the curvature at 9.1 GPa, when the c/a axial ratio passes through a special value $\sqrt{3}$. This, the so-called c/a anomaly, has also been found for Cd under pressure.⁶ One of the possible explanations for the anomaly is the electronic topological transition (ETT), which involves a topological change of the Fermi surface. The ETT occurs when a new Fermi surface appears or an existing Fermi surface disappears with application of external perturbationlike pressure. Experimental evidence for the ETT of Zn under high pressure was first given by Potzel *et al.* as an anomaly in the Mössbauer spectra of Zn at 6.6 GPa at low temperature.^{7,8} The sudden drop of the Lamb-Mössbauer factor at this pressure was related to the ETT. The c/a axial ratio at the anomaly in the Mössbauer spectra is estimated to be close to $\sqrt{3}$, if one considers the thermal expansion of Zn.⁵ Hence the c/a anomaly can be related to the ETT. However later x-ray study on Cd under pressure⁶ showed that the c/a anomaly also occurs at the same special value of $\sqrt{3}$. Since there is no reason to assume that the ETT's of Zn and Cd take place at the same axial ratio, Takemura proposed a universal change in the bonding properties of the hcp structure at $c/a = \sqrt{3}$.⁶ The hcp structure has spe-

cial symmetry both in real and reciprocal spaces at $c/a = \sqrt{3}$.

These experimental results stimulated subsequent total-energy calculations on Zn and Cd at high pressures.⁹⁻¹² The calculations employed different approximations for exchange and correlation interactions and are not consistent to each other specifically on the shape of the Fermi surface at high pressures. Nevertheless all of the calculations suggest that the ETT takes place in Zn at high pressures and the c/a axial ratio anomalously changes at the ETT. The calculated c/a anomaly, however, never appears at $c/a = \sqrt{3}$.

Neutron inelastic-scattering experiments have also been done on Zn at high pressure at room temperature. Morgan *et al.* support the ETT model,¹³ while Klotz *et al.* have observed no anomaly nor softening in the phonon frequency of Zn under pressure.^{14,15} So far the existence of the ETT and its correlation to the c/a anomaly are still controversial.

In the present paper we show that the previously reported c/a anomaly in Zn disappears when helium is used as a pressure-transmitting medium. The c/a anomaly is most probably induced by the nonhydrostaticity of the methanol-ethanol-water (MEW) pressure-transmitting medium (16:3:1 by volume) used in the previous studies. We will discuss the existence of the ETT in Zn under high pressure on the basis of the present new x-ray data.

High pressure was generated with a diamond-anvil cell (DAC) having diamond anvils of 600- μm culet size. A fine powder of Zn (99% purity) is the same as that used in the previous studies,^{5,6} and has an average particle size of 4 μm .

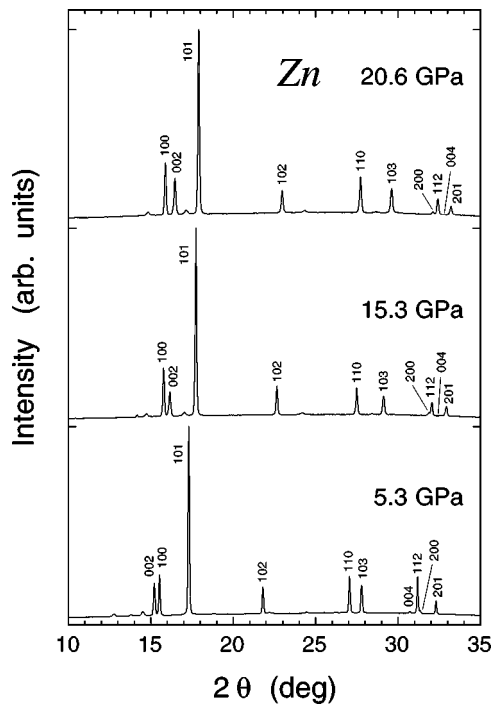


FIG. 1. Powder x-ray-diffraction patterns of Zn under pressure with He-pressure medium. The x-ray energy was 20.00 keV. Weak unindexed peaks are of ZnO formed on the surface of Zn powder. Note that the 002 reflection is clearly observed even at 20.6 GPa, indicating that good hydrostaticity is retained up to the highest pressure.

The powder was lightly pressed into a thin plate of 15 μm thickness. A small piece (100 \times 100 μm) was cut from the plate and put in a spring steel gasket (110- μm thickness after indentation and 200- μm hole diameter) together with ruby chips for pressure measurement. The sample thickness was small enough compared with the final thickness of the gasket (\sim 30 μm) at high pressures, thereby ensuring good hydrostaticity. Helium was loaded to the DAC at room temperature with a high-pressure gas-loading system operating at a gas pressure of 180 MPa.¹⁶ The sample pressure was determined on the basis of the ruby pressure scale.¹⁷

An angle-dispersive powder x-ray-diffraction experiment has been carried out at room temperature on the bending magnet beam line 18C of the Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK). The x-ray was monochromatized to 20.00 keV. Diffracted x rays were detected with an imaging plate. Details of the experimental setup and the data analysis have been described elsewhere.¹⁸

Figure 1 shows representative x-ray-diffraction patterns of Zn at high pressures. One notices that the 002 reflection is clearly observed even at the highest pressure of 20.6 GPa. This is in contrast to the previous studies,^{5,6} in which the 002 reflection is hardly observed above 10 GPa. The disappearance of the 002 reflection in the previous studies indicates a strong preferred orientation of the specimen under uniaxial compression. The 002 planes of hcp metals easily slip and are orientated preferentially under uniaxial stress. In the present diffraction geometry incident x rays are parallel to the compression axis (perpendicular to the diamond faces). Therefore, if the 002 planes lie parallel to the diamond faces

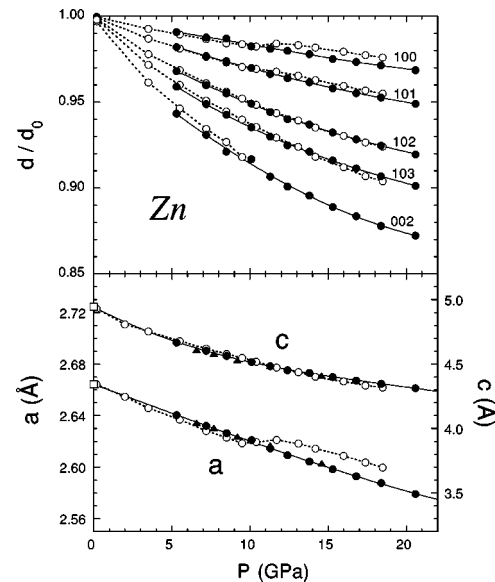


FIG. 2. The change in the d spacings (top) and lattice parameters (bottom) of Zn under high pressure. The d spacings are normalized to the values at atmospheric pressure d_0 . The solid circles are with the He-pressure medium in the present study, and the open circles are the data with the MEW medium in the previous study (Ref. 6). The 110 reflection shows similar change as the 100 reflection and is omitted in the figure for clarity. Only the data on increasing pressure are shown on the top panel, while the solid triangles on the bottom panel show the data with the He-pressure medium on decreasing pressure. Open squares on the bottom panel indicate the lattice parameters at atmospheric pressure from literature (Ref. 23). Note the different scale for the a and c axes.

due to the preferred orientation, they do not diffract the x rays. The evolution of the nonhydrostaticity was also evident in the broadening of x-ray-diffraction peaks as well as of ruby fluorescence peaks. The nonhydrostaticity was induced by the solidification of the MEW pressure medium above 10 GPa.¹⁹ Helium solidifies at 11.5 GPa at room temperature,²⁰ but we observed no evidence of nonhydrostaticity to at least 20.6 GPa: the intensity of the 002 reflection remains nearly constant (see Fig. 1), and the x-ray and ruby peaks show no broadening. Solid He is soft enough in this pressure range.²¹ These facts indicate that good hydrostaticity is retained in the present experiment.²²

Figure 2 (top) shows the variation with pressure of the d spacings normalized to the values at atmospheric pressure d_0 . The figure compares two experimental runs, one with the He medium in the present study and the other with the MEW medium in the previous study.⁶ All the d spacings smoothly change in the case of the He medium, while the d spacings with the MEW medium show a small expansion at around 10 GPa. The expansion is largest for the 100 reflection, and hence gives rise to the corresponding expansion of the a axis (Fig. 2, bottom). Consequently the volume dependence of the c/a axial ratio with the MEW medium shows an anomalous change as shown in Fig. 3. The anomaly in the axial ratio is located very close to the special value $c/a = \sqrt{3}$ and has been interpreted as a singularity in the hcp structure.^{5,6} However, since there is no anomaly with the He-pressure medium, the anomaly in the previous studies is most likely induced by the solidification of the MEW-pressure medium. The present

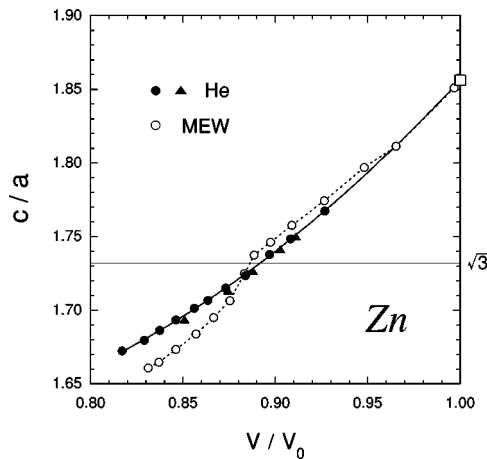


FIG. 3. The change in the axial ratio of Zn as a function of the relative volume. The solid circles (triangles) show the data on increasing (decreasing) pressure with the He-pressure medium in the present study. The open circles are the data on increasing pressure with the MEW medium in the previous study (Ref. 6). The open square indicates the axial ratio at atmospheric pressure from literature (Ref. 23). The curves are drawn for the guide of eyes.

data with He-pressure medium are perfectly reversible with respect to pressure without any hysteresis.

It is now well established how a crystal lattice deforms under uniaxial stress.²⁴ When the pressure medium solidifies, the specimen is compressed uniaxially with two diamond anvils. Lattice planes lying perpendicular to the compression axis are more compressed compared with the hydrostatic case, whereas planes parallel to the compression axis are expanded (Fig. 4). Since the direction of incident x rays is parallel to the compression axis in the present diffraction geometry, we always measure the diffracted x rays from the lattice planes lying nearly parallel to the compression axis. The d spacings measured under uniaxial stress are therefore larger than the values measured under hydrostatic conditions. The expansion of the d spacings under uniaxial stress can be estimated from the elastic constants of Zn following the procedure given in Ref. 24. Although the elastic constants of Zn at high pressures are not available in literature, an estimation based on the elastic constants at atmospheric pressure and their pressure derivatives²⁵ well explains the observed deviation of the d spacings in the case of the MEW medium.

The MEW medium is reported to remain hydrostatic up to 14.5 GPa in literature.¹⁹ This was the basis of the previous

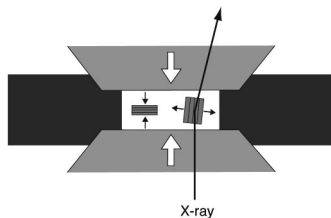


FIG. 4. Deformation of a crystal compressed uniaxially in a diamond-anvil cell. Lattice planes lying perpendicular to the compression axis (left) are more compressed compared with the hydrostatic case, whereas those lying parallel to the compression axis (right) are relatively expanded. Incident x rays are diffracted only by the planes lying nearly parallel to the compression axis in the present diffraction geometry.

interpretation of the c/a anomaly to be different from the effect of nonhydrostaticity.⁶ The reason is unclear why the MEW medium developed nonhydrostaticity at a pressure much lower than 14.5 GPa. The MEW medium is easy to evaporate, thereby possibly changing the ratio of methanol, ethanol, and water enclosed in the gasket hole. A small change in the mixing ratio from 16:3:1 drastically lowers the hydrostatic limit.¹⁹ Further, it is difficult to understand the result on Cd that the anomaly also occurred at $c/a = \sqrt{3}$ and at a pressure of 12.5 GPa, higher than the case of Zn.⁶ We suspect that the mixing ratio of MEW might be closer to the ideal one in this case. The solidification pressure was then higher than the case of Zn, making the c/a ratio at the solidification nearly $\sqrt{3}$. X-ray-diffraction experiments on Cd with He pressure medium should be done in order to clarify this point. In any case the occurrence of the c/a anomaly at $\sqrt{3}$ seems to be accidental.

In order to examine the possibility that the c/a anomaly appears only under nonhydrostatic conditions, we have carried out a comparative experiment with isopropyl alcohol as a pressure medium. Isopropyl alcohol solidifies at 4.3 GPa, above which nonhydrostaticity develops.²⁶ Measured lattice parameters showed continuous deviation from those with He medium above 4.3 GPa, but there was no definitive change in the c/a ratio at this pressure nor at around 9.1 GPa. From this we infer that the previous c/a anomaly is most likely induced by the rapid hardening of the MEW-pressure medium after solidification.

An important argument is why the theoretical calculations reproduced the c/a anomaly, which is now proved to be an artifact. It would be reasonable to assume that Zn undergoes ETT's at high pressures, as the Fermi surface should change the topology under compression. If an ETT takes place, thermodynamic quantities are expected to show anomalous change.²⁷ At room temperature, however, the ETT can be smeared out due to thermal fluctuations, and accordingly the anomaly in the axial ratio could be extremely small. Internal stress inherent to polycrystalline aggregate under pressure can also mask such a small anomaly.²² The absence of the c/a anomaly in the present experiment, therefore, does not imply the absence of the ETT in Zn. It should be noted that the most recent theoretical work points out that the previously observed c/a anomaly is too strong compared with the theoretical anomaly based on a single ETT.¹² High-precision single-crystal x-ray diffraction at high pressure and low temperature with He would be the best one to see whether any anomaly may appear in Zn. It is also important to detect the ETT experimentally with a direct probe.

In summary the present study reveals that there is no anomaly in the volume dependence of the axial ratio of Zn at room temperature. The previously reported c/a anomaly is most likely induced by the solidification of the pressure medium. The present results, however, do not preclude the possible ETT in Zn under pressure, since the ETT would be smeared out at room temperature and difficult to detect. Direct measurements of the change in the Fermi surface of Zn under pressure at low temperature are desirable.

The author would like to thank Dr. T. Kikegawa for his help on the beam line 18C. The present work has been done under Proposal No. 97G269 of the Photon Factory.

- *Electronic address: takemura@nirim.go.jp
- ¹W. A. Harrison, Phys. Rev. **129**, 2512 (1963).
- ²J. A. Moriarty, Phys. Rev. B **10**, 3075 (1974); **16**, 2537 (1977).
- ³J. Hafner and V. Heine, J. Phys. F **13**, 2479 (1983).
- ⁴D. Singh and D. A. Papaconstantopoulos, Phys. Rev. B **42**, 8885 (1990).
- ⁵K. Takemura, Phys. Rev. Lett. **75**, 1807 (1995).
- ⁶K. Takemura, Phys. Rev. B **56**, 5170 (1997).
- ⁷W. Potzel, M. Steiner, H. Karzel, W. Schiessl, M. Köfferlein, G. M. Kalvius, and P. Blaha, Phys. Rev. Lett. **74**, 1139 (1995).
- ⁸M. Steiner, W. Potzel, H. Karzel, W. Schiessl, M. Köfferlein, G. M. Kalvius, and P. Blaha, J. Phys.: Condens. Matter **8**, 3581 (1996).
- ⁹L. Fast, R. Ahuja, L. Nordström, J. M. Wills, B. Johansson, and O. Eriksson, Phys. Rev. Lett. **79**, 2301 (1997).
- ¹⁰D. L. Novikov, A. J. Freeman, N. E. Christensen, A. Svane, and C. O. Rodriguez, Phys. Rev. B **56**, 7206 (1997).
- ¹¹B. K. Godwal, S. Meenakshi, and R. S. Rao, Phys. Rev. B **56**, 14 871 (1997).
- ¹²D. 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).
- ¹³J. G. Morgan, R. B. Von Dreele, P. Wochner, and S. M. Shapiro, Phys. Rev. B **54**, 812 (1996).
- ¹⁴S. Klotz, M. Braden, and J. M. Besson, Phys. Rev. Lett. **81**, 1239 (1998).
- ¹⁵A. W. Overhauser, Phys. Rev. Lett. **81**, 4022 (1998).
- ¹⁶K. Takemura, P. Ch. Sahu, Y. Kunii, and Y. Toma (unpublished).
- ¹⁷H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).
- ¹⁸O. Shimomura, K. Takemura, H. Fujihisa, Y. Fujii, Y. Ohishi, T. Kikegawa, Y. Amemiya, and T. Matsushita, Rev. Sci. Instrum. **63**, 967 (1992).
- ¹⁹I. Fujishiro, G. J. Piermarini, S. Block, and R. G. Munro, in *High Pressure in Research and Industry*, Proceedings of the 8th AIR-APT Conference Uppsala, edited by C. M. Backman, T. Johansson, and L. Tegner (ISBN, Sweden, 1982), Vol. II, p. 608.
- ²⁰J. M. Besson and J. P. Pinceaux, Science **206**, 1073 (1979).
- ²¹P. M. Bell and H. K. Mao, Year Book-Carnegie Inst. Washington **80**, 404 (1981).
- ²²It is known that a compact polycrystalline sample can in principle develop internal stress even under hydrostatic conditions, if crystal grains are directly touching each other without a pressure medium in between. Since it is difficult to observe the microscopic grain boundaries of the actual specimen under high pressure, the current experiment may not yet offer ideal data for Zn under truly hydrostatic conditions. However, the present data show no detectable evidence of nonhydrostaticity as is argued in the text, and hence, should be considered as nearly truly hydrostatic data for polycrystalline Zn.
- ²³J. Donohue, *The Structures of the Elements* (Wiley, New York, 1974), p. 225.
- ²⁴See, for example, A. K. Singh, J. Appl. Phys. **73**, 4278 (1993); T. Uchida, N. Funamori, and T. Yagi, *ibid.* **80**, 739 (1996); A. K. Singh, C. Balasingh, H.-K. Mao, J. Shu, and R. J. Hemley, Rev. High Pressure Sci. Technol. **7**, 205 (1998).
- ²⁵H. M. Ledbetter, J. Phys. Chem. Ref. Data **6**, 1181 (1977).
- ²⁶G. J. Piermarini, S. Block, and J. D. Barnett, J. Appl. Phys. **44**, 5377 (1973).
- ²⁷I. M. Lifshitz, Zh. Éksp. Teor. Fiz. **38**, 1569 (1960) [Sov. Phys. JETP **11**, 1130 (1960)].