Powder x-ray diffraction study on mercury up to 200 GPa

K. Takemura[1,*], *S. Nakano*[1], *and Y. Ohishi*[2]

[1]*National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0044 Japan*

[2]*Japan Synchrotron Radiation Research Institute (JASRI), Mikazuki, Hyogo 679-5198 Japan*

**E-mail: takemura.kenichi@nims.go.jp*

Introduction

Liquid mercury solidifies at about 1.2 GPa at room temperature. The solid phase, called α, has a simple rhombohedral structure (Donohue 1974). The α phase transforms to the β phase with a body-centered tetragonal structure at 3.4 GPa, and to the γ phase with an orthorhombic structure at about 12 GPa (Schulte and Holzapfel 1993). At 37 GPa, the δ phase with the hexagonal-close-packed (hcp) structure appears. The δ phase is reported to be stable to at least 67 GPa (Schulte and Holzapfel 1996). The stability of the δ phase is particularly interesting in view of the structural relationship to the similar hcp phases of Zn and Cd (Takemura 1997). A first-principles calculation predicts a wide stability range for the δ phase up to 1 TPa (Moriarty 1988). The purpose of the present study is to investigate experimentally the stability of the δ phase at ultrahigh pressures.

Experimental methods

High-pressure powder x-ray diffraction experiments were carried out with a diamond-anvil cell (DAC). Sample preparation was done in a globe box filled with argon. A small droplet of liquid mercury was solidified on a plate cooled by liquid nitrogen. The solid mercury was then transferred on the gasket and closed in the DAC, which was also cooled on the cold plate. Pressures were determined from the lattice parameters of a Pt pressure marker (Holmes *et al.* 1989). Diffraction experiments were done at room temperature by using monochromatic x rays with a wavelength of 0.4125 Å and an imaging plate or an x-ray CCD camera on the beam line BL10XU of SPring-8. A diamond backing plate was used to collect the full diffraction rings (Takemura and Nakano 2003).

Results and discussion

Two experimental runs were done up to a maximum pressure of 193 GPa. The δ phase was found to be stable over the whole pressure range investigated. Figure 1 shows the diffraction pattern at 193 GPa. The lattice parameters at this pressure are a = 2.612(3) and c = 4.284(7) Å, which give c/a = 1.640(3) and the relative volume V/V_0 = 0.514(1).

Figure 2 shows the change of the c/a axial ratio of the δ phase with pressure. The axial ratio is quite large after the γ-δ transition (1.75), being comparable with 1.86 of Zn and 1.89 of Cd at atmospheric pressure. At higher pressures, the axial ratio smoothly decreases in the same manner as Zn and Cd under high pressure (Takemura 1997). Figure 3 shows the pressure-volume relationship. We have fitted the Birch-Murnaghan equation

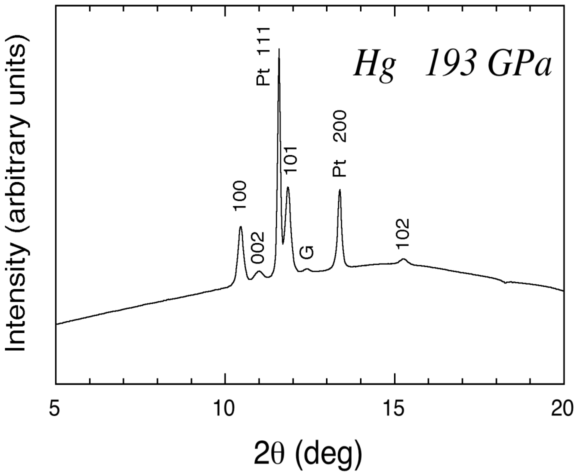

Fig. 1. Powder x-ray diffraction pattern of the high-pressure δ phase of Hg at 193 GPa. Diffraction peaks of the Pt pressure marker and the Re gasket (G) are present.

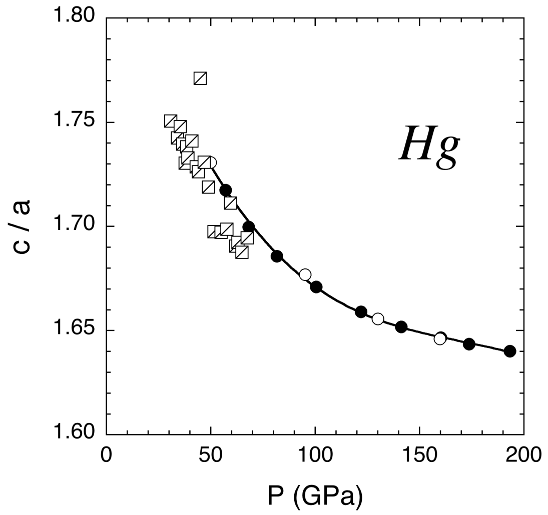

Fig. 2. Pressure dependence of the *c/a* axial ratio of δ-Hg. Open and closed circles indicate the present data in two different runs, and squares from the literature (Schulte and Holzapfel 1993).

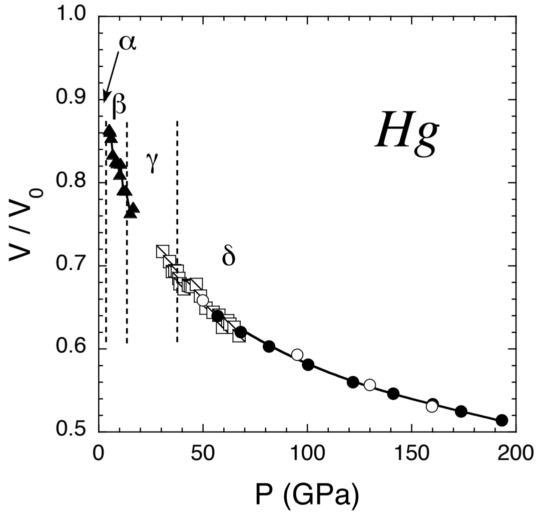

Fig. 3. Equation of state for Hg. Open and closed circles are the present data in two different runs, triangles from our previous experiment (Takemura and Aoki 1987), and squares by Schulte and Holzapfel (1993).

of state to the present pressure-volume data. For high-pressure phases, it is better to use the bulk modulus and its pressure derivative at a reference pressure as fitting parameters, rather than to use those at atmospheric pressure (Holzapfel 2001). This is due to the large uncertainty in volume of the high-pressure phase extrapolated to atmospheric pressure. By setting the reference pressure at 50 GPa, we have obtained the bulk modulus and its pressure derivative as 292(13) GPa and 5.5(5), respectively.

Conclusion

We have extended the pressure range of investigation on Hg to about 200 GPa, three times higher than the previous studies. The δ phase was found to be stable up to the highest pressure, confirming the theoretical prediction. The bulk modulus, its pressure derivative, and the change of the *c/a* axial ratio with pressure have been determined.

References

Donohue J., 1974. *The Structures of the Elements*. New York: Wiley.

Holmes N. C., Moriarty J. A., Gathers G. R., Nellis W. J., 1989. The equation of state of platinum to 660 GPa (6.6 Mbar). *J. Appl. Phys.* **66**, 2962-2967.

Holzapfel W. B., 2001. Equation of state for high pressure phases. *Rev. High Press. Sci. Technol.* **11**, 55-58.

Moriarty J. A., 1988. High-pressure structural phase stability in Hg to 1 TPa (10 Mbar). *Phys. Lett.* A **131**, 41-46.

Schulte O., Holzapfel W. B., 1993. Phase diagram for mercury up to 67 GPa and 500 K. *Phys. Rev. B* **48**, 14009-14012.

Schulte O., Holzapfel W. B., 1996. Effect of pressure on the atomic volume of Zn, Cd, and Hg up to 75 GPa. *Phys. Rev. B* **53**, 569-580.

Takemura K., Aoki K., 1987. (unpublished.)

Takemura K., 1997. Structural study of Zn and Cd to ultrahigh pressures. *Phys. Rev. B* **56**, 5170-5179.

Takemura K., Nakano S., 2003. Performance of a synthetic diamond backing-plate for the diamond-anvil cell at ultrahigh pressures. *Rev. Sci. Instrum.* **74**, 3017-3020.