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Isotope effects on the physicochemical properties of zirconium hydride

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Abstract

The isotope effects on the physicochemical properties of zirconium hydride have been studied. The zirconium deuteride specimens in the form of pellets (6-mm diameter×10 mm length) were loaded with deuterium contents with 1.5–1.7 D/Zr, and were fabricated directly from zirconium metal in a modified UHV Sieverts apparatus. The X-ray diffraction analysis showed that all the zirconium deuterides prepared exhibited CaF_2-type structure(δZrD_{2-x}), and the lattice parameter of δZrD_{2-x} was smaller than that of δZrH The zirconium deuteride had higher elastic moduli than the hydride. The microhardness of the zirconium deuteride was slightly higher than that of hydride. The physicochemical properties of the zirconium deuteride such as Debye temperature and heat capacity were estimated from the sound velocities and the thermal expansion data. The Debye temperature and heat capacity of zirconium deuteride were higher than that of zirconium hydride.

Keywords: Zirconium deuteride; Isotope effect; Lattice constant; Thermal expansion coefficient; Elastic modulus; Hardness; Debye temperature; Heat capacity

1. Introduction

Zirconium alloys have been employed as the nuclear materials of fission reactors such as LWRs and CANDUs. Problems such as hydrogen embrittlement of the cladding and the pressure tube have stirred interest in the characteristics of zirconium hydride and deuteride. It is important to understand the physicochemical properties of zirconium hydride and deuteride and the isotope effects. Therefore, the physicochemical properties of zirconium deuteride such as mechanical and thermal properties have been measured and the isotope effects of zirconium hydride were discussed in the present study.

2. Experimental

The zirconium deuteride specimens in the form of pellets were directly fabricated from zirconium metal with 99.9% purity in a modified UHV Sieverts apparatus. The deuterium contents of the specimens range from 1.5 to 1.7 D/Zr.

The lattice parameters and thermal expansion coefficients were obtained by high-temperature X-ray diffraction analysis. The sound velocities were measured by means of a ultrasonic pulse-echo method, and the elastic moduli were evaluated. The hardness was also measured. The Debye temperatures and heat capacities were estimated from these results.

3. Results and discussion

The results of the X-ray diffraction analysis at room temperature showed that all the zirconium deuterides prepared in the present study had the δ phase with a fluorite-type structure. In Fig. 1, the lattice parameter of zirconium deuteride obtained in the present study is indicated, together with the reported data [1–8]. As is obvious in this figure, the lattice parameter of the zirconium deuteride is smaller than that of the hydride and slightly increases with the deuterium content. The change in the lattice parameter with the deuterium content C_D is expressed in the following relationship:

$$a_D(\mathrm{nm}) = 0.4738 + 1.961 \times 10^3 C_D(\mathrm{D/Zr})$$

As shown in Fig. 2, the average thermal expansion coefficients estimated from the high- temperature X-ray diffraction range from 2×10^{-5} to $3\times10\ \mathrm{K}^{-1}$. The thermal expansion coefficients increased with the deuterium con-

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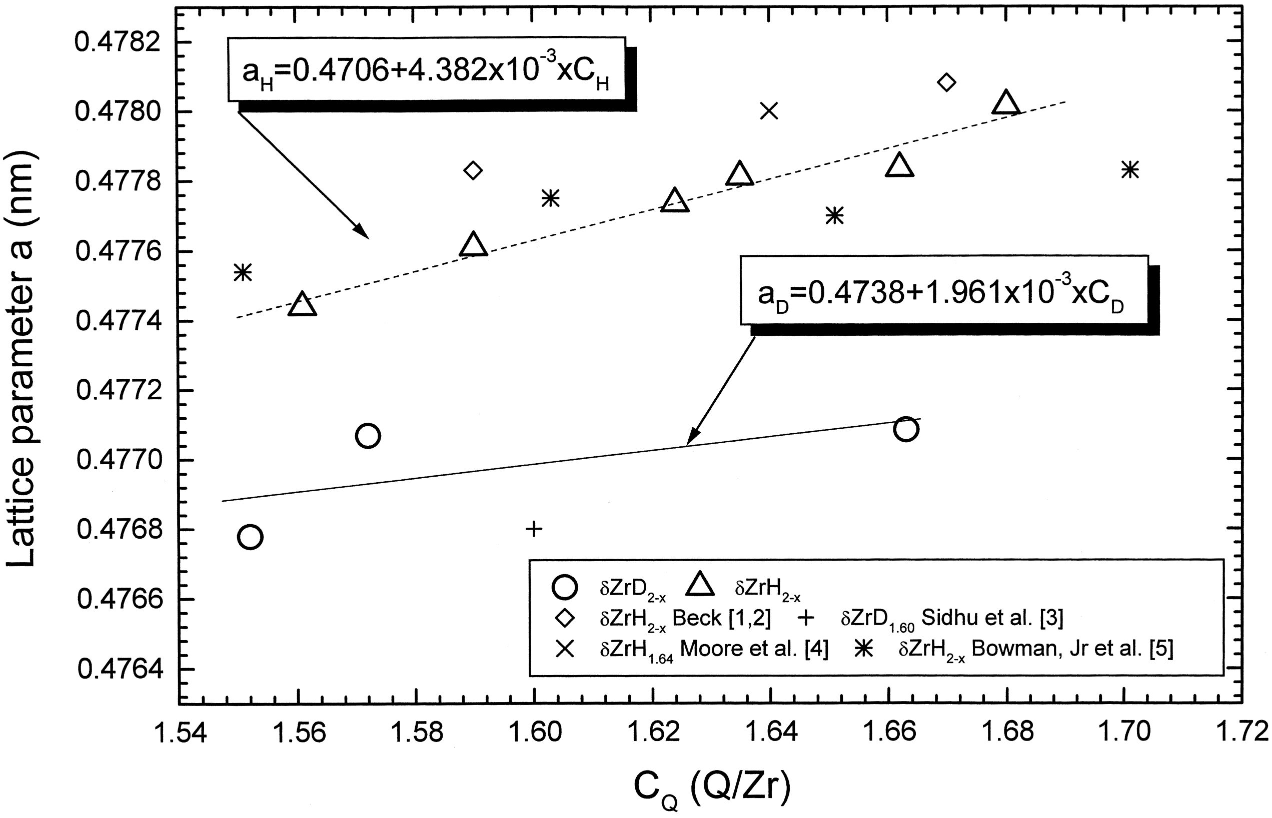

Fig. 1. Change in the lattice parameter a of δZrD_{2-x} with the deuterium content C_D.

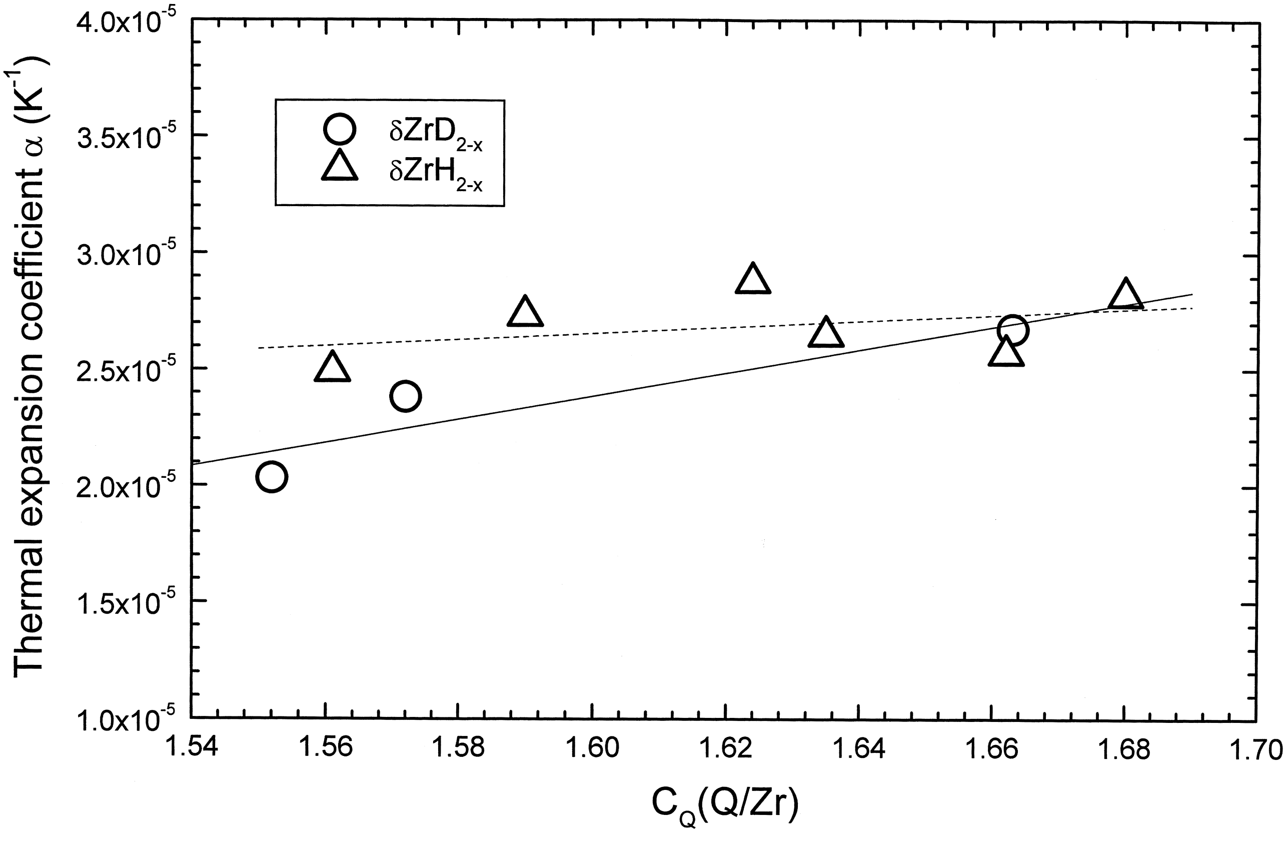

Fig. 2. Change in the thermal expansion coefficient α of δZrD_{2-x} with the deuterium content C_D.

tents. There was no marked difference in the thermal expansion coefficient between the hydride and the deuteride.

Longitudinal and shear sound velocities at room temperature differed from the hydrides to the deuterides. The shear modulus G, Young's modulus E, bulk modulus K and Poisson's ratio v were estimated from the longitudinal sound velocity and the shear sound velocity. Both Young's and shear moduli of the deuteride are larger than those of the hydride and slightly decrease with increasing deuterium content, as shown in Figs. 3 and 4. Poisson's ratio of the deuteride was estimated to be about 0.26, irrespective of deuterium content, and lower than that of the hydride.

The microhardness values obtained for the deuteride shown in Fig. 5 are slightly larger than those of the hydrides and decrease with increasing deuterium content. The variation in microhardness of the deuteride with the deuterium contents can be written as:

$$H_v^D 5.22 - 1.33 x C_D (D/Zr).$$

It is known that the microhardness is related to Young's modulus for various materials. For pure metals, we estimated the relation of hardness H_v with Young's modulus E [9], as indicated in Fig. 6. For oxide and carbide ceramics, the H_v value is also proportional to the E value, and the value of H_v/E is 0.05 [10], much larger than those for pure metals. As evidenced by this figure, the zirconium hydrides and deuterides reveal the intermediate characteristics between ceramics and metals, and show the same linear relationship.

The Debye temperatures Θ_D for the zirconium deuterides estimated from the longitudinal sound velocity and shear sound velocity are shown in Fig. 7. The Debye temperature for the zirconium deuteride is higher than that of the hydride, and decreases with increasing deuterium content C_D. This suggests that the zirconium lattice vibration is influenced by the hydrogen isotope.

The heat capacity C_p^D for the zirconium deuteride can be approximately estimated from the sum of various contributions:

$$C_p^D(\mathrm{J/mol/K}) = C_v^{Zr} + C_d + C_{el} + C_v^D$$

where the C_v^{Zr} is the vibrational term for the acoustic mode, the C_d is the dilatational term, the C_{el} is the electronic term, and C_D is the vibrational term for the optical mode.

On the assumption that only zirconium atoms appears to contribute to the acoustic mode of the lattice vibrations of the zirconium hydride and deuteride, the vibrational term

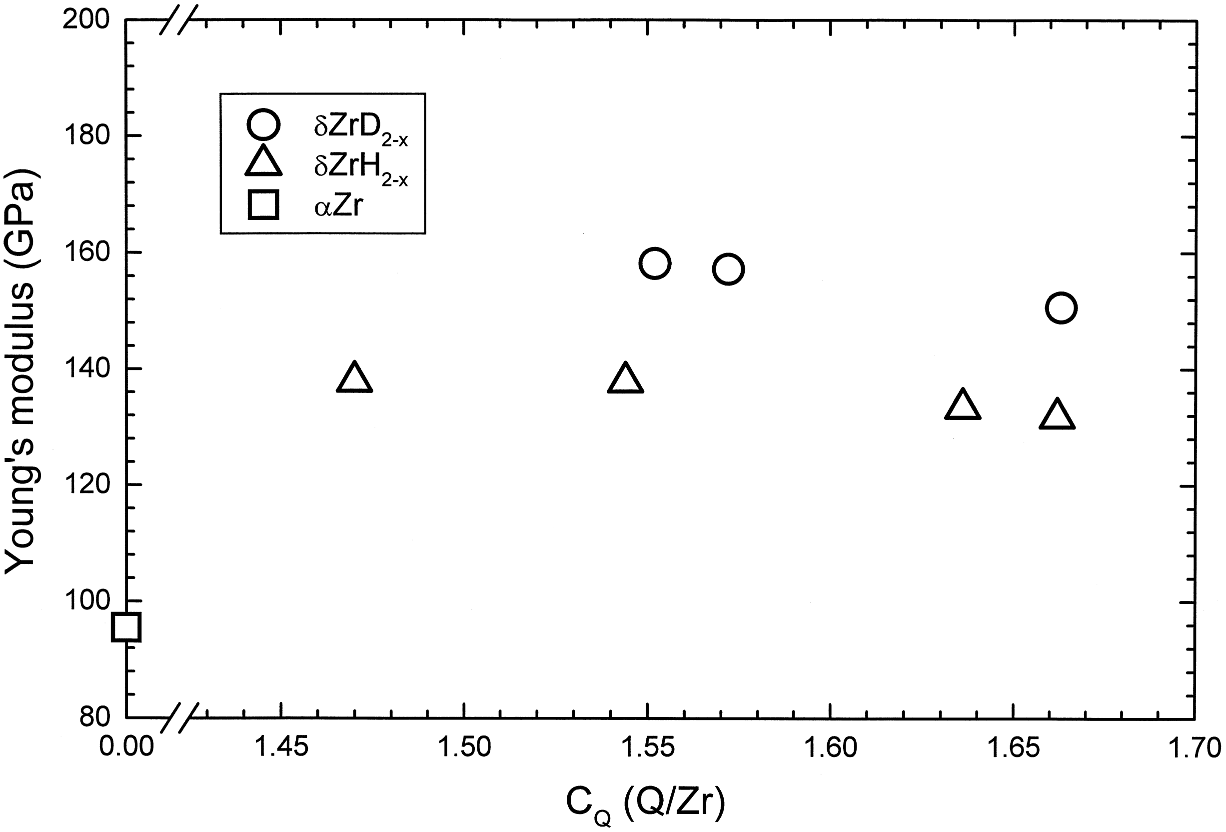

Fig. 3. Change in Young's modulus E of δZrD_{2-x} with the deuterium content C_D.

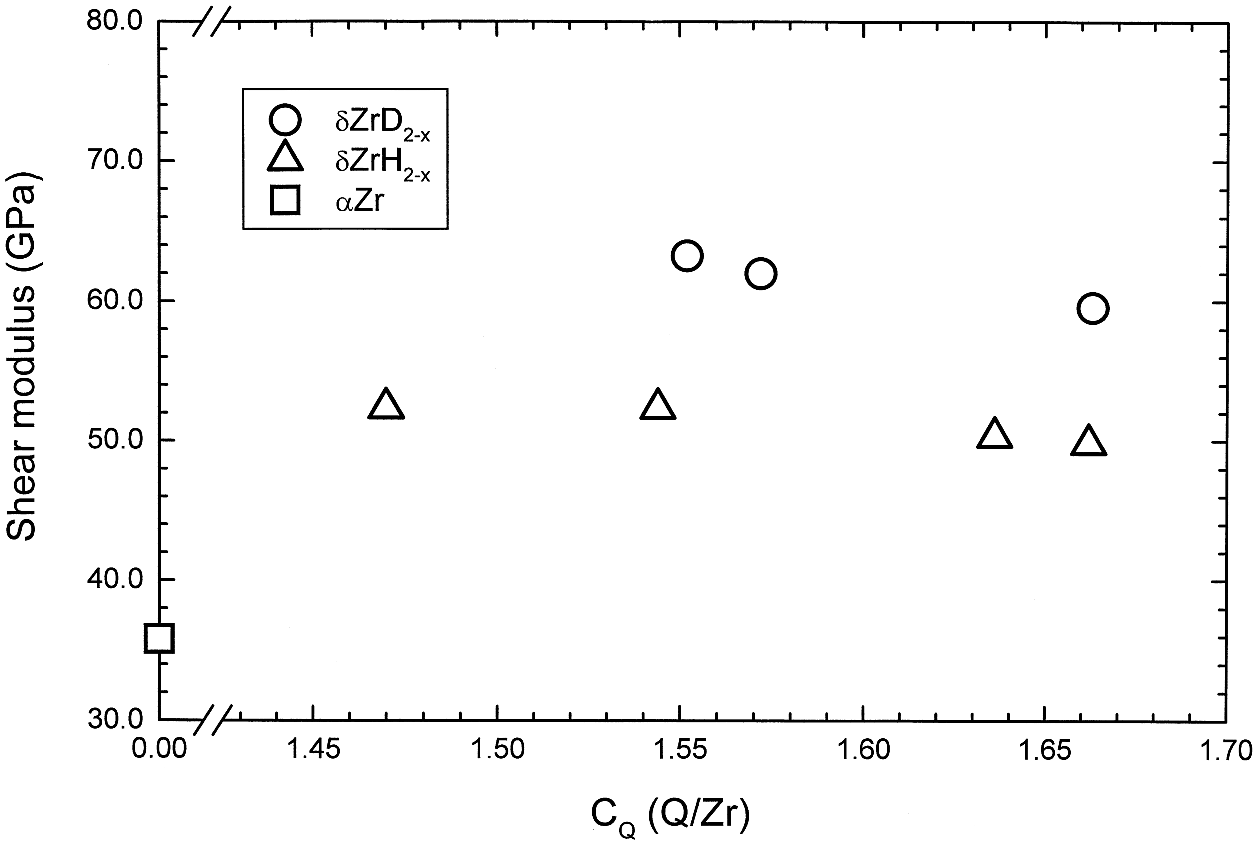

Fig. 4. Change in the Shear modulus G of δZrD_{2-x} with the deuterium content C_D.

for the acoustic mode was estimated. The dilatational term was estimated using the experimental data of the thermal expansion coefficient, the compressibility and the molar volume for the deuteride. The electronic term C_{el} was estimated using the coefficient of electronic heat capacity $\gamma = 4.10 \times 10^{-3}$ J/mol/K^2 reported for $\varepsilon ZrH_{2.00}$ [11], since there exists no experimental data of the electronic heat capacity for δ zirconium hydride and deuteride. The vibration of deuterium in the zirconium deuteride mainly contributes to the vibrational term for the optical mode. Assuming that hydrogen or deuterium behaves as harmonic oscillators in the zirconium hydride and deuteride, we calculated the vibrational term for the optical mode. For the calculation, we estimated the vibration frequency of deuterium ν_D from:

$$\nu_D = \nu_H / \sqrt{2}$$

using the literature value for the vibrational frequency of hydrogen $\nu_H = 3.31 \times 10^{13}$ s^{-1} obtained by neutron scattering measurement for δZrH_{15} [12]. The vibrational term for the optical mode C_v^D was evaluated from the following equation:

$$C_v^D = 3 n_D R (\Theta_E / T)^2 \exp(\Theta_E / T) / [\exp(\Theta_E / T) - 1]^2$$

In this equation, $\Theta_E = h\nu_D / k$ is the Einstein temperature of deuterium in the zirconium deuteride, and n_D is the number of deuterium atoms per molecule.

Fig. 8 shows the temperature dependence of heat capacity C_P estimated for the zirconium deuteride. At lower temperature, there exists no marked difference in the heat capacity between hydride, deuteride and pure zirconium. This implies that zirconium lattice vibration mainly determines the heat capacity of zirconium hydride and deuteride. Above room temperature, the heat capacity of the deuteride C_P^D is much larger than that of the hydride C_P^H. At a given temperature, the heat capacity increases with the deuterium content. The optical mode significantly contributes to the heat capacity at higher temperatures. The variation in the heat capacity with the deuterium contents and temperature can be given by the empirical equation:

$$\begin{aligned} C_P^D = {} & 24.33 + 16.35 \times C_D \\ & + (-7.724 \times 10^{-4} + 1.236 \times 10^{-2} x C_D) T \\ & - (2.255 \times 10^5 + 8.905 \times 10^5 \times C_D) / T^2. \end{aligned}$$

In Fig. 9, the heat capacity for the deuteride estimated in the present study is compared with the experimental data reported in the literature [11–13]. The estimated heat capacity of the deuteride well agrees with the reported values.

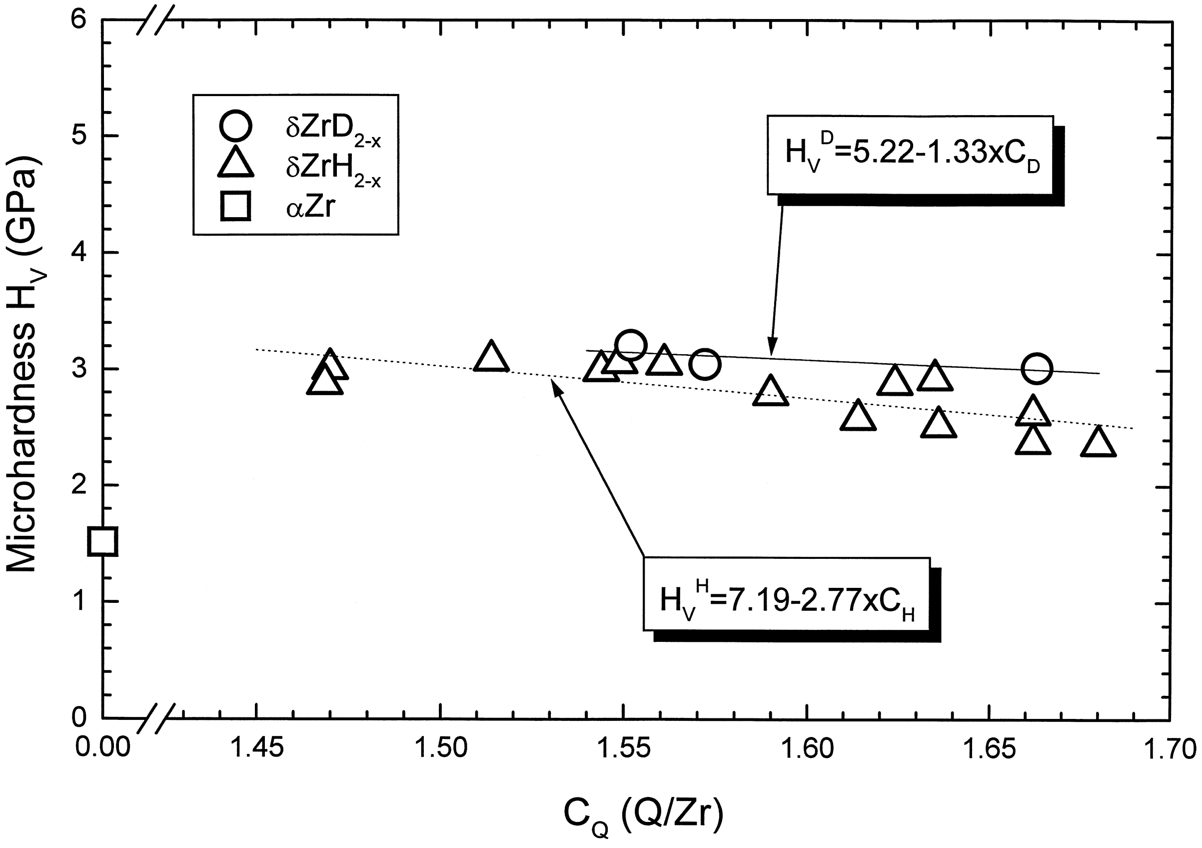

Fig. 5. Change in the microhardness H_v of δZrD_{2-x} with the deuterium content C_D.

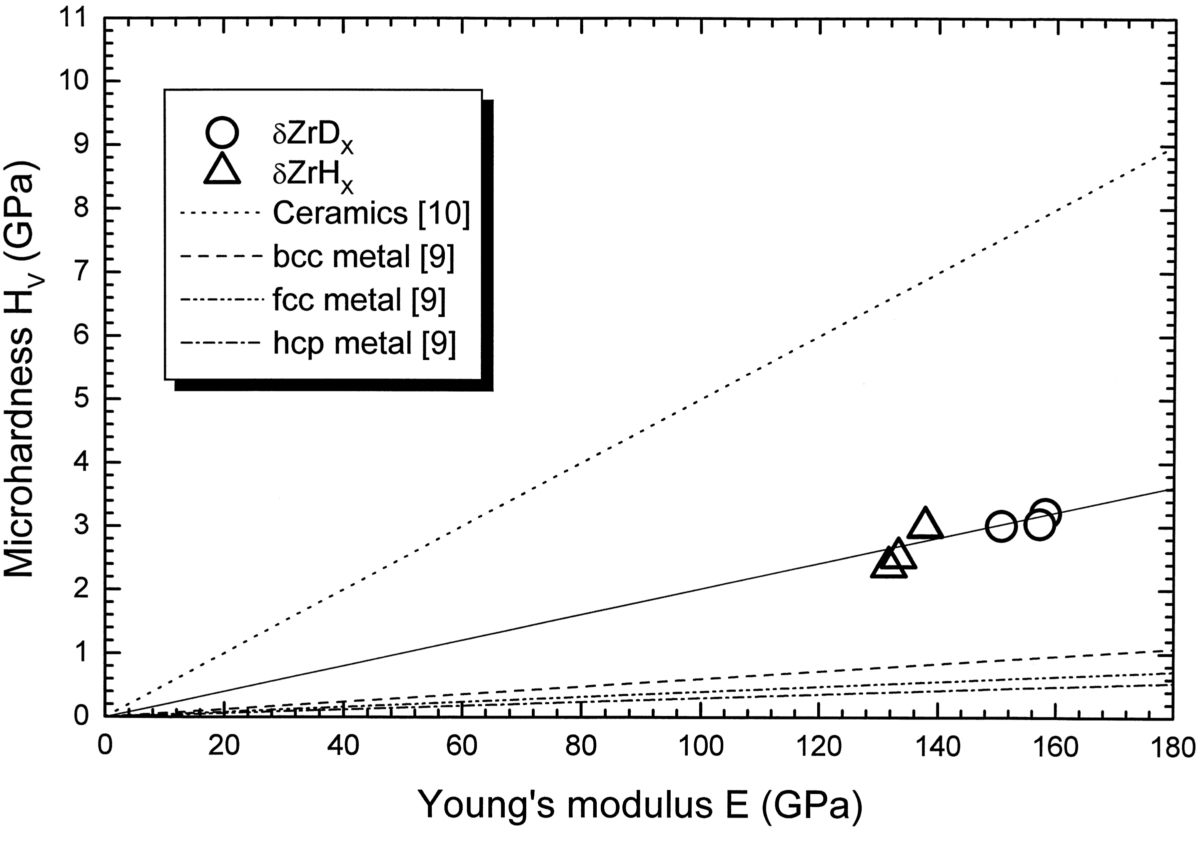

Fig. 6. Relationship between microhardness H_v and Young's modulus E for δZrD_{2-x}.

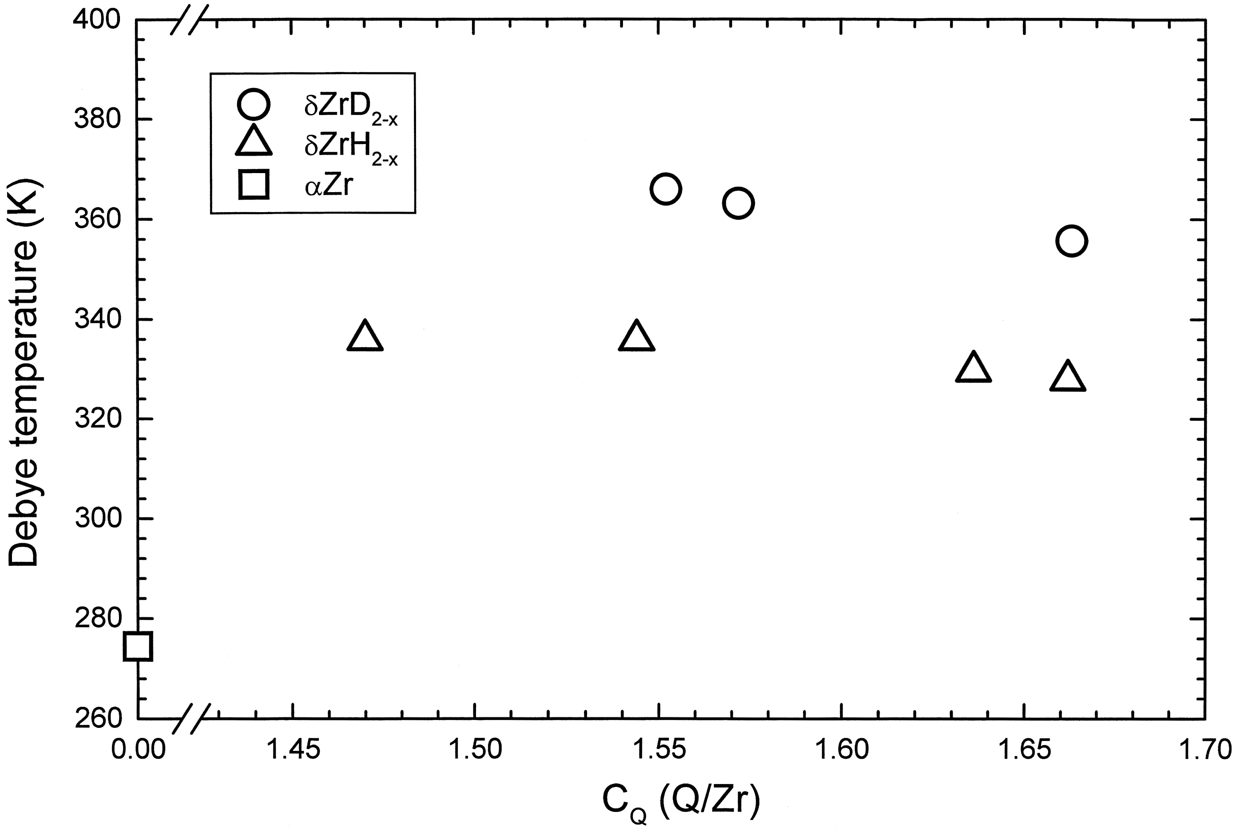

Fig. 7. Change in the Debye temperature Θ_D of δZrD_{2-x} with the deuterium content C_D.

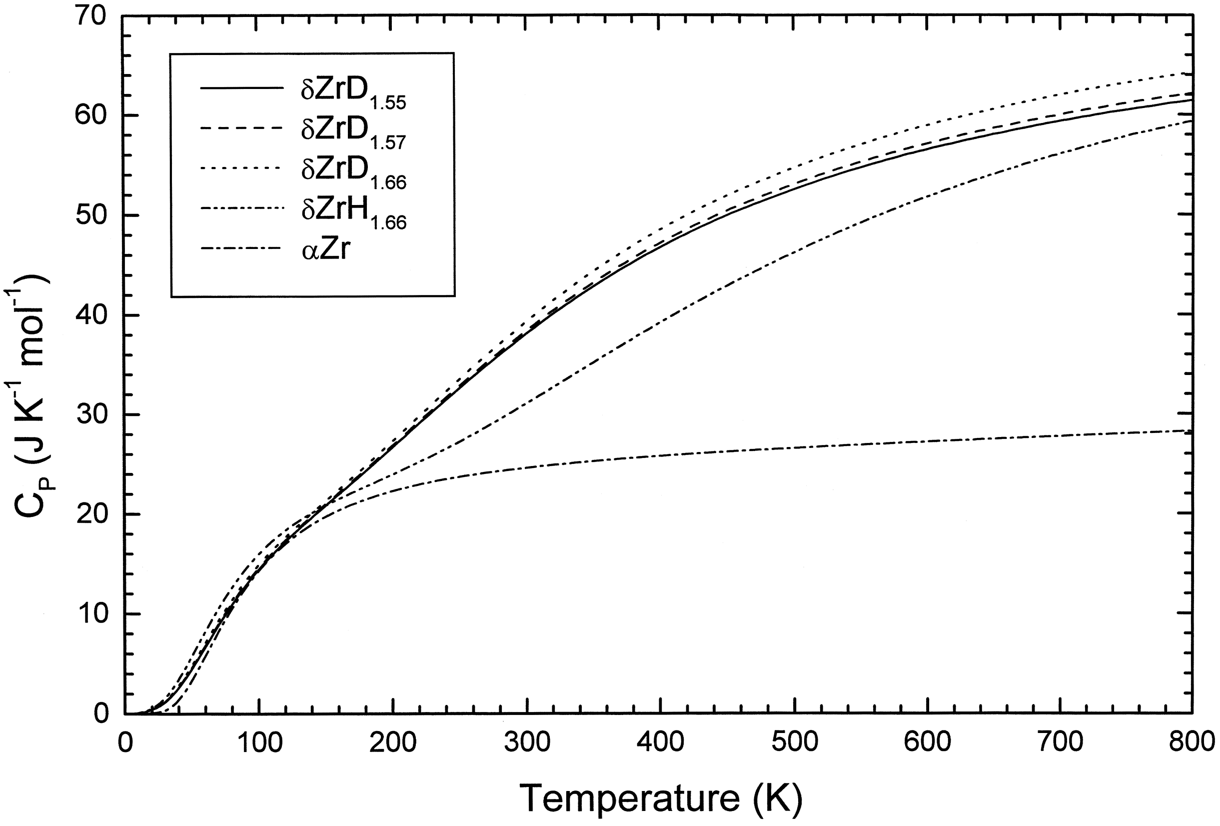

Fig. 8. Temperature dependence of heat capacity C_P^D of δZrD_{2-x}.

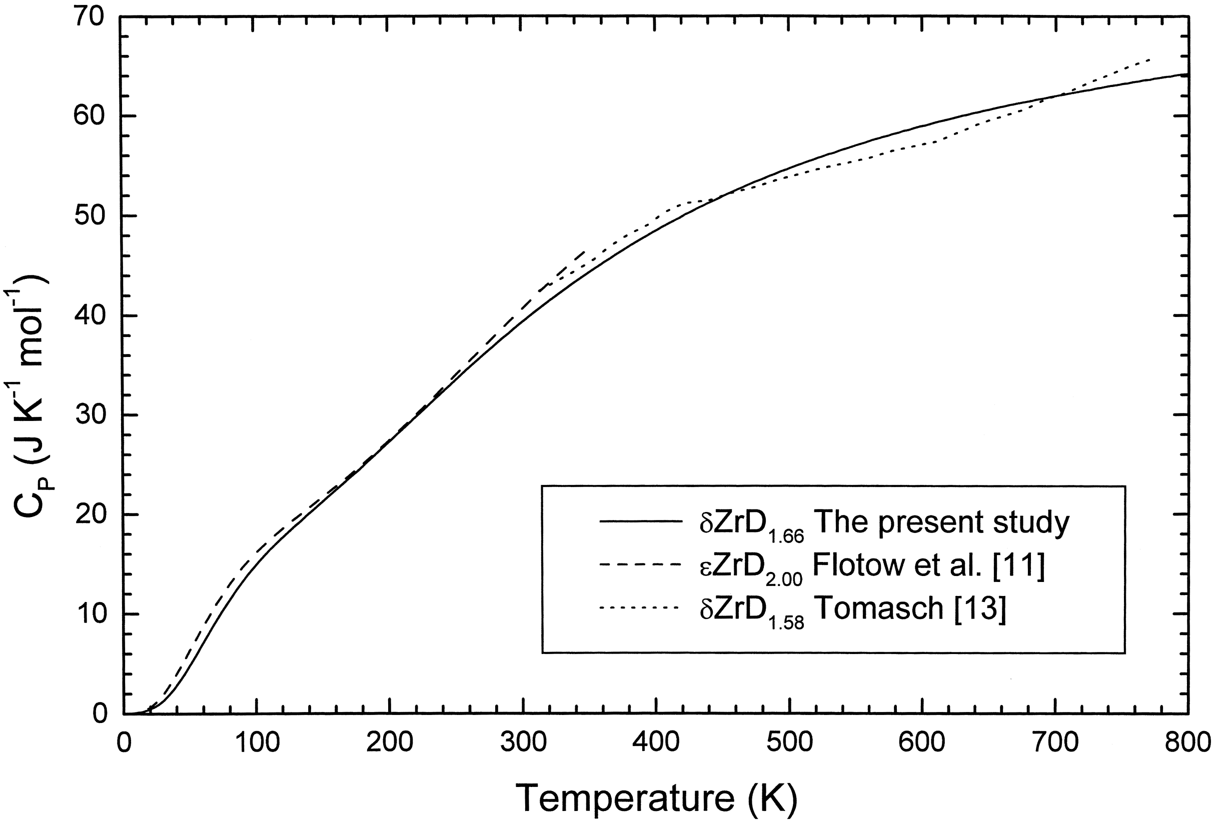

Fig. 9. Temperature dependence of heat capacity C_P^D of $\delta ZrD_{1.66}$.

4. Conclusions

The lattice parameter of the CaF_2-type zirconium deuteride δZrD_{2-x} was much smaller than that of the hydride δZrH_{2-x} and increased with the deuterium content. The thermal expansion coefficient of the zirconium deuteride was larger than that of the hydrides. The zirconium deuteride had higher Young's and shear moduli than the hydride. The hardness value of the deuteride was slightly higher than that of the hydride and decreased with increasing deuterium content. The Debye temperature of the zirconium deuteride was higher than that of zirconium hydride. The heat capacity estimated from the sound velocities and the thermal expansion data was in good agreement with the experimental data reported in the literature.

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References

[1] C.P. Kempter, R.O. Elliott, K.A. Schneider Jr., J. Chem. Phys. 33 (1960) 837.
[2] F. Ducastelle, R. Caudron, P. Costa, J. Phys. 31 (1970) 57.
[3] R.L. Beck, Am. Soc. Met. Trans. Q 55 (1962) 542.
[4] R.L. Beck, Am. Soc. Met. Trans. Q 55 (1962) 556.
[5] S.S. Sidhu, N.S.S. Murthy, F.P. Campos, D.D. Zauberis, Adv. Chem. Ser. 39 (1963) 87.
[6] K.E. Moore, W.A. Young, J. Nucl. Mater. 27 (1968) 316.
[7] J.S. Cantrell, R.C. Bowman Jr., D.B. Sullenger, J. Phys. Chem. 88 (1984) 918.
[8] R.C. Bowman Jr., B.D. Craft, J.S. Cantrell, E.L. Venturini, Phys. Rev. B 31 (1985) 5604.
[9] S. Yamanaka, K. Yamada, T. Tuzuki, M. Katsura, M. Hoshino, W. Saiki, J. Alloys Comp. (1998) in press.
[10] K. Tanaka, H. Koguchi, T. Mura, Int. J. Eng. Sci. 27 (1989) 11.
[11] H.E. Flotow, D.W. Osborne, J. Chem. Phys. 34 (1961) 1418.
[12] W.L. Whittemore, A.W. McReynolds, Phys. Rev. 113 (1958) 806.
[13] W.J. Tomasch, Phys. Rev. 123 (1961) 510.