Solubility and diffusivity of hydrogen and deuterium in α-hafnium at high temperatures

Shizuo Naito, Masahiro Yamamoto and Tomoyasu Hashino

Institute of Atomic Energy, Kyoto University, Uji, Kyoto 611, Japan

Abstract. The solubility and diffusivity of hydrogen and deuterium in polycrystalline α-hafnium have been measured at temperatures of 873–1873 K. The ratios of the solubility and diffusivity of deuterium to those of hydrogen are explained assuming that hydrogen and deuterium in hafnium are anharmonic oscillators. The activation energy for the diffusion of hydrogen and deuterium is found to be 0.46 ± 0.02 eV.

1. Introduction

Hafnium is a metal of practical importance not only because it has a high melting point and can be a starting material for ceramics with a high melting point but also because it can absorb a large amount of hydrogen under an appropriate condition (Beck and Mueller 1968, Paetz and Sperner 1976, Kubaschewski 1981). It is also a metal of interest, because the hafnium–hydrogen system is, at small hydrogen concentrations, expected to retain the host-lattice structure (HCP, α-phase) up to about 2010 K (Paetz and Sperner 1976, Kubaschewski 1981) and provides an opportunity to study the behaviour of hydrogen in the single phase over a wide range of temperatures. Despite these facts, there exist only a small number of reports on hydrogen in hafnium. This paper concerns an attempt to investigate the solubility and diffusivity of hydrogen isotopes in hafnium and, in particular, to find the factors which influence the differences between the solubilities and diffusivities of hydrogen and deuterium at high temperatures.

Some investigators have reported measurements of the solubility of hydrogen and deuterium in hafnium (Edwards and Veleckis 1962, Ricca and Giorgi 1970, Watanabe 1985, Yura et al 1986). All these measurements were made at temperatures of less than 1150 K. Some of these measurements (Ricca and Giorgi 1970, Watanabe 1985) show that the ratio of the solubility of deuterium to that of hydrogen deviates from the ratio calculated assuming that hydrogen and deuterium in hafnium are independent harmonic oscillators. No reasonable explanations of this deviation seem to have appeared yet. For some metals other than hafnium, however, several investigators have discussed the effects of anharmonicity associated with vibrations of the hydrogen isotopes on the solubility and its difference between the hydrogen isotopes (Katz et al 1971, Lässer and Powell 1986) as well as on other properties of the metal–hydrogen isotope systems such as phase transitions and elastic constants (Flanagan et al 1985, Oppeneer et al 1988). Evidence for the anharmonicity has been given (Eckert et al 1983, Rush et al 1984). The anharmonicity is expected also for the hydrogen isotopes in hafnium.

There are almost no reports on the measurements of the diffusion of the hydrogen isotopes in hafnium; only the activation energy for the diffusion of hydrogen and deuterium in HfH_x and HfD_x ($x \simeq 2$) has been reported (Pope *et al* 1981, Forker *et al* 1986). Theoretical studies show that, among the various mechanisms of diffusion of the hydrogen isotopes in metals, the over-barrier jump mechanism is dominant at high temperatures (Kehr 1978, Fukai and Sugimoto 1985). The anharmonicity plays an important role in diffusion by over-barrier jumps as well as in the solubility. The effects of the anharmonicity on the diffusion have been studied both experimentally and theoretically (Katz *et al* 1971, Franklin 1975, Jacucci *et al* 1987).

In this investigation we measure the solubility and diffusivity of hydrogen and deuterium over the temperature range 873–1873 K and show that the result can be explained using rate theory if we make a modification to include the anharmonicity of the vibrations of the hydrogen isotopes. We briefly discuss the experimental result using alternative modifications.

2. Experiment

The apparatus and methods to measure the solubility and diffusivity are the same as those described previously (Naito 1983, Naito *et al* 1984). Briefly, hydrogen and deuterium in a chamber (hydrogen reservoir) of known volume were admitted to a chamber (sample chamber) containing a sample heated to a given temperature with the pressure in the sample chamber kept constant at a given value. We obtained the diffusivity from the change in the pressure in the hydrogen reservoir with time, and the solubility from the pressure in the hydrogen reservoir after the diffusion was completed. We obtained the solubility also from the equilibrium pressure after admitting a known amount of hydrogen and deuterium without controlling the pressure in the sample chamber.

The samples were spherical polycrystalline hafnium of diameters 10 and 11 mm, having a nominal purity of 99.97% excluding 3% zirconium. Before the measurements the samples were heated to about 1900 K for more than 5 h at a pressure of less than 10^{-7} Pa. This heat treatment ensures measurement of the diffusivity free from the effect of surface contamination. In fact, in our secondary-ion mass spectroscopy analysis of zirconium, which chemically resembles hafnium, made at 1023 K and at about 10^{-7} Pa, we found only a small amount of negative chlorine ions and a trace of negative sulphur ions, both of which were segregated from the bulk (Yamamoto *et al* 1989). In addition, the diffusivity of hydrogen in zirconium measured under a similar ultra-high-vacuum condition was not appreciably different from the diffusivity measured using the methods independent of the effect of the surface (Naito 1983).

In the diffusivity measurement by the method of absorption, it is crucial to obtaining an accurate diffusivity to eliminate the effect of the surface on the absorption rate, particularly the effect in the early stage of absorption. Since hydrogen dissociatively dissolves into hafnium and the hydrogen atoms in hafnium are rather mobile, the rate at which hydrogen crosses the surface is, in the early stage of the absorption, proportional to the hydrogen pressure (Glasstone *et al* 1941), which is proportional to the square of the equilibrium concentration of the hydrogen atoms at the surface. On the other hand, the rate at which the hydrogen atoms at the surface move into the bulk is related to the concentration of the hydrogen atoms at the surface. The rate at which hydrogen crosses the surface, therefore, becomes relatively large as the pressure increases and, at high
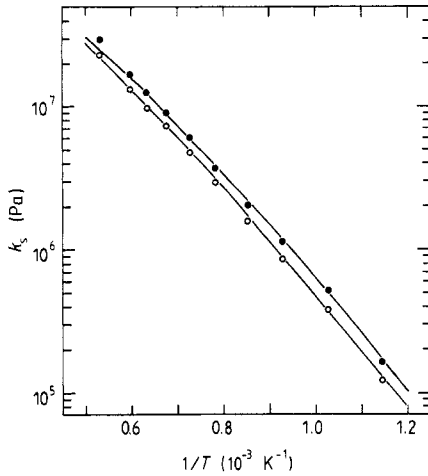
Figure 1. The Arrhenius plot of k_{Hs} and k_{Ds}: ○, hydrogen; ●, deuterium; ——, computed from equation (5).
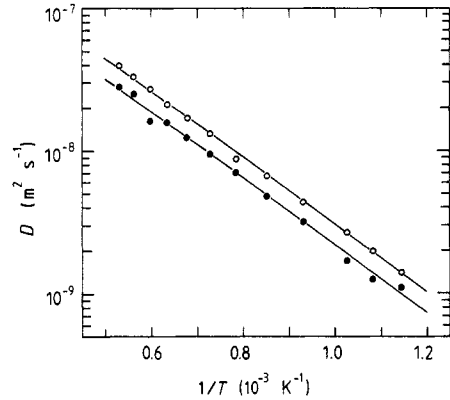
Figure 2. The Arrhenius plot of D_H and D_D: ○, hydrogen; ●, deuterium; ——, computed from equation (6).

pressures, diffusion controls the absorption rate. This has been confirmed by the absorption of hydrogen in zirconium (Naito 1983). Thus we measured the diffusivity at 1.1 Pa in this investigation. At pressures lower by one order of magnitude, the diffusivity obtained from the absorption rate was pressure dependent.

The presence of phase boundaries can have an influence on the solubility and diffusivity near the phase boundaries. To avoid this, we carried out measurements at 873 K at hydrogen concentrations less than half the solubility limit ($[H/Hf] \simeq 5 \times 10^{-2}$) of α-hafnium (Edwards and Veleckis 1962) and at smaller concentrations at higher temperatures. A pressure of 1.1 Pa, at which the diffusivity was measured, corresponds to a concentration well below the solubility limit.

Figure 1 shows the measured solubility and figure 2 shows the measured diffusivity.

3. Solubility and diffusivity

We can consider the solubility in terms of rate theory. Assuming the hydrogen isotopes to be ideal in the gas phase, we have (Glasstone *et al* 1941), if the concentration of the hydrogen isotope in the metal is small,

$$p = k_s \theta^2 \tag{1}$$

where

$$k_s = cT(f_g/f_i^2) \exp(-\varepsilon_s/kT) \tag{2}$$

p is the pressure of hydrogen, θ is the concentration of hydrogen in hafnium, c is a constant independent of temperature, f is the partition function of the hydrogen isotope, ε_s is the heat of solution and k is Boltzmann's constant. The subscripts g and i denote the hydrogen isotopes in the gas phase and in the metal, respectively. We calculate f_i assuming that the hydrogen isotope occupies a tetrahedral site in α-hafnium as it does in α-titanium and α-zirconium (Khoda-Bakhsh and Ross 1982). We also assume that

the c/a ratio is ideal although it is 1.581 and is smaller by about 3% than the ideal ratio. The potential V for the tetrahedral site (Eckert et al 1983) can be written as

$$V = \tfrac{1}{2}m\omega_x^2(x^2 + y^2) + \tfrac{1}{2}m\omega_z^2 z^2 + \alpha z(x^2 - y^2) + \beta_x(x^4 + y^4) + \beta_z z^4 + \beta_{xy}x^2 y^2$$
$$+ \beta_{yz}(y^2 + x^2)z^2 \tag{3}$$

where m is the mass of the hydrogen isotope, ω_x is the angular frequency in the x and y directions, ω_z is the angular frequency in the z direction and α, β_x, β_z, β_{xy} and β_{yz} are constants. The x and y directions have been chosen to be parallel to the two edges (of the tetrahedron) which do not cross each other and the z direction to be perpendicular to both the x and y directions. The change in the c/a ratio accompanying hydrogen absorption is so small $(c/a = 1.581$ at $\theta = 0$ and $c/a = 1.582$ at $\theta = 0.136$ (Kubaschewski 1981)) that we regard V as concentration independent. V is also assumed to be isotope independent as in the palladium–hydrogen isotope systems (Rush et al 1984). The energy $E_{n_x n_y n_z}$ of the hydrogen isotope vibrating in the potential can be calculated, where n_x, n_y, $n_z = 0, 1, 2, \ldots$. Its explicit form is given in the Appendix. Thus we have the partition function

$$f_i = \sum_{n_x, n_y, n_z} \exp\left(-\frac{E_{n_x n_y n_z}}{kT}\right). \tag{4}$$

The partition function f_g for hydrogen in the gas phase includes the freedom of translation and rotation in addition to that of vibration. Thus we have

$$k_s = c'T^{7/2}m^{5/2}[\{1 - (\varphi_g/2T)[\sinh(\hbar\omega_g/2kT)]^{-2}\exp(-\varphi_g/2T)\}/\sinh(\hbar\omega_g/2kT)]$$
$$\times (1/f_i^2)\exp(-\varepsilon_s/kT) \tag{5}$$

where c' is a constant independent of temperature, ω_g is the angular frequency of the vibration of hydrogen atoms and φ_g is a constant characterising the anharmonicity of the vibration, the energy of which is expressed as $E_n = \hbar\omega_g(n + \tfrac{1}{2}) - k\varphi_g(n + \tfrac{1}{2})^2$. The difference between the solubilities of hydrogen and deuterium can be expressed by the ratio k_{Ds}/k_{Hs}. The subscripts H and D are used to denote the quantities corresponding to hydrogen and deuterium, respectively. Since the potential is isotope independent, we use the relation $\omega_{Dx}/\omega_{Hx} = \omega_{Dy}/\omega_{Hy} = (\tfrac{1}{2})^{1/2}$ and $\varepsilon_{Ds}/\varepsilon_{Hs} = 1$ when computing k_{Ds}/k_{Hs}.

Diffusion by over-barrier jumps can be described with the diffusion coefficient (Glasstone et al 1941)

$$D = dT(f_i^\ddagger/f_i)\exp(-\varepsilon_d/kT) \tag{6}$$

where d is a constant independent of temperature and ε_d is the activation energy for the diffusion. The superscript $\ddagger$ denotes the quantities corresponding to the activated state. In view of the fact that a hydrogen atom occupying a tetrahedral site in the HCP structure can make a diffusion jump to another tetrahedral site only through a kind of site different from the tetrahedral site (Anderson et al 1984), we choose as a possible activated state the state of the hydrogen atom occupying an octahedral site. If the terms including z are excluded from equation (3), it is a potential that corresponds to two-dimensional motion of the hydrogen atom occupying the octahedral site and is used to calculate f_i. The directions of x, y and z, however, are different from those used for the potential of the tetrahedral site. When calculating D_D/D_H, we assume that $\omega_{Dx}^\ddagger/\omega_{Hx}^\ddagger = (\tfrac{1}{2})^{1/2}$ and $\varepsilon_{Dd}/\varepsilon_{Hd} = 1$ in addition to the assumption made in the case of the solubility, and consider $\omega_x^\ddagger/\omega_x$ a parameter to be determined.
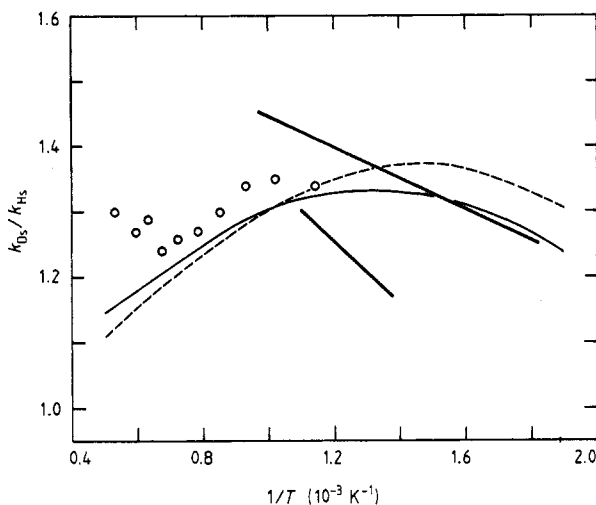
Figure 3. The Arrhenius plot of k_{Ds}/k_{Hs}: ○, present study: ———— (upper), calculated from the experimental data of Ricca and Giorgi (1970); ———— (lower), calculated from the experimental data of Watanabe (1985); ————, computed from equation (5) with $\hbar\omega_{Hx} = 158$ meV, $\frac{3}{2}\beta_x(\hbar/m\omega_x)^2 = 9.0$ meV, $\beta_x = \beta_z$ and $\beta_{xy} = \beta_{yz} = 0$; ---, computed from equation (5) with $\hbar\omega_{Hx} = 151$ meV and $\alpha = \beta_x = \beta_z = \beta_{xy} = \beta_{yz} = 0$.

4. Results and discussion

Figure 3 shows a comparison of k_{Ds}/k_{Hs} obtained from the measurement of p and θ with k_{Ds}/k_{Hs} computed from equation (5). At temperatures around 900 K, the measured values fall between those obtained by Ricca and Giorgi (1970) and those obtained by Watanabe (1985). The values used to compute equation (5) are $\hbar\omega_{Hg} = 545$ meV, $\hbar\omega_{Dg} = 387$ meV, $k\varphi_{Hg} = 14.6$ meV and $k\varphi_{Dg} = 7.9$ meV. No measurement of $\hbar\omega_x$ or $\hbar\omega_z$ is found for hafnium, and we have regarded it as a parameter to be determined. The potential V involves five coefficients and it is difficult to determine their values uniquely. The fitting of the computed curve (thin full curve in figure 3) to the measured values results in $\hbar\omega_x = 158$ meV and $\frac{3}{2}\beta_x(\hbar/m\omega_x)^2 = 9.0$ meV when $\omega_x = \omega_y = \omega_z, \beta_x = \beta_z$ and $\alpha = \beta_{xy} = \beta_{yz} = 0$, i.e. when we have an isotropic harmonic oscillator. The value $\frac{3}{2}\beta_x(\hbar/m\omega_x)^2 = 9.0$ meV does not seem unreasonable when compared with the values of 13.4 meV for nickel (Katz *et al* 1971) and 19 meV for palladium (Rush *et al* 1984). $\hbar\omega_x$, $\hbar\omega_y$ and $\hbar\omega_z$ may have different values as reported for the yttrium–hydrogen system (Anderson *et al* 1988), but we obtain a curve which is almost the same as that obtained for $\omega_x = \omega_y = \omega_z$ if their average is 158 meV. We cannot determine their values uniquely only from the comparison of the computed curve with the experimental result of this investigation. Other choices for the coefficients in V can give a similar curve; if we put, for example, all the coefficients except α equal to zero, a similar curve is obtained. However, it should be noted that the anharmonicity plays an important role in interpreting the solubility. The curve (thin full curve in figure 3) computed using equation (3) leads to better agreement with the experimental result than the curve (broken curve) computed using the potential without the anharmonicity, i.e. only the quadratic terms of equation (3).

Here we note another possible way to explain the experimental result. It can be shown that a simpler model reproduces the experimental result if the potential in which the hydrogen isotope vibrates is allowed to be isotope dependent. We assume that a hydrogen isotope is a collection of three independent one-dimensional anharmonic oscillators and that only the anharmonic terms in the potential are isotope dependent. The experimental result is reproduced to the same extent as shown above when the energy due to the anharmonic terms is larger by 17% for deuterium than for hydrogen, i.e. when the energy due to the potential is larger by about 1% for deuterium than for hydrogen. The solubility above 1573 K in particular is reproduced by this model better than shown above. Thus the isotope dependence of the potential can influence the isotope effect of the solubility. However, no evidence for the isotope dependence of the potential has been found for the hydrogen isotope in hafnium. For palladium, for example, no isotope dependence has been shown for hydrogen and deuterium (Rush *et al* 1984, Oppeneer *et al* 1988). It seems that detailed neutron scattering data are necessary for further discussion of the models.

Some other attempts to reproduce the experimental result are briefly discussed. First, we assume that $\omega_{Dx}/\omega_{Hx} \neq (\frac{1}{2})^{1/2}$, as has been considered by Oates and Flanagan (1977). A small change in ω_{Dx}/ω_{Hx} causes k_{Ds}/k_{Hs} to change considerably, but it is impossible to find a value of ω_{Dx}/ω_{Hx} which can reproduce the measured values both at 873 K and at 1873 K. Inclusion of the linear dependence of ω_{Dx}/ω_{Hx} on the hydrogen isotope concentration (Flanagan *et al* 1985) turns out to improve the fit only slightly. Second, we allow some of the hydrogen atoms in hafnium to move freely at high temperatures. In fact, assuming that they obey the Boltzmann distribution, we find that, at 1873 K, more than 20% have an energy larger than 0.46 eV, which is the activation energy for the diffusion of hydrogen in hafnium. However, the partition function for oscillation combined with that for free motion (Oates and Flanagan 1977), if their ratio is calculated according to the Boltzmann distribution, was not capable of reproducing the experimental results at high temperatures; the partition function for free motion causes k_{Ds}/k_{Hs} to decrease too much as the temperature increases. Third, relaxing the restriction $\varepsilon_{Ds}/\varepsilon_{Hs} = 1$ and considering the linear dependence of $\varepsilon_{Ds}/\varepsilon_{Hs}$ on the hydrogen concentration are as unsuccessful as the first attempt.

We show in figure 1 a comparison of measured k_s and k_s computed from equation (5) using the values of ω_x, ω_z, α, β_x, β_{xy} and β_{yz} determined above. The measured k_s lies on a smooth and almost straight line (not shown in figure 1). This confirms the expectation that only the α-phase is present under our experimental conditions. At each temperature, the measured pressures and concentrations follow equation (1) with a fluctuation in k_s less than $\pm 5\%$. This fluctuation comes mainly from that in the measured pressures. From the Arrhenius plot of the measured k_s the heat ε_s of solution is found to be 0.71 ± 0.01 eV, which is in approximate agreement with the values reported by Edwards and Veleckis (1962), Ricca and Giorgi (1970) and Watanabe (1985). The curves computed using equation (5) are shown by the thin full curves, from which we find $\varepsilon_s = 0.82$ eV. This value is larger by about 0.1 eV than the value of 0.71 eV obtained from the direct Arrhenius plot of the measured k_s because the temperature is involved in the pre-exponential factor in equation (5).

In figure 4, the measured D_D/D_H-values are compared with those computed from equation (6). The measured D_D/D_H slightly exceed $(m_D/m_H)^{-1/2}$. In computing equation (6) we employ the values already determined and make the assumption described in the preceding section. The coefficients of the potential for the activated state are chosen as $\frac{3}{2}\beta_x(\hbar/m\omega_x)^2 = 9.0$ meV and $\beta_{xy} = 0$, which are the same values as those used when
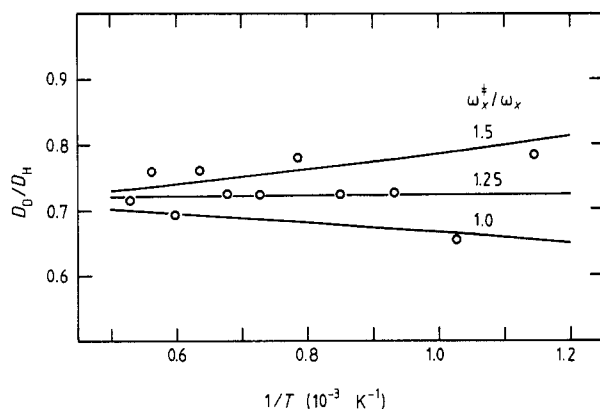
Figure 4. The Arrhenius plot of D_D/D_H: ——, computed from equation (6) using the values of $\omega_x^\ddagger/\omega_x$ shown.

k_{Ds}/k_{Hs}-values were computed. The choice of the values of β_x and β_{xy} involves arbitrariness as mentioned above. It is possible to choose as the activated state a state other than the hydrogen atom occupying the octahedral site, but the arbitrariness involved in determining the potential makes it difficult to choose the activated state. From the fitting of the curve we find that $\omega_x^\ddagger/\omega_x = 1.25$, which suggests that the hydrogen isotopes are more tightly bound in the activated state than in the equilibrium state. D_D/D_H-values are shown in figure 4 for two other values of $\omega_x^\ddagger/\omega_x$; the effect of $\omega_x^\ddagger/\omega_x$ becomes pronounced as the temperature decreases.

We obtain from figure 2 the activation energy for the diffusion of hydrogen and deuterium. The measured diffusion coefficients lie, up to 1873 K, on almost completely straight lines, from which we have $\varepsilon_d = 0.46 \pm 0.02$ eV. This value is in the range of ε_d for HfH_x and HfD_x ($x \simeq 2$) (Pope *et al* 1981, Forker *et al* 1986) and α-titanium and α-zirconium (Paetz and Sperner 1976, Naito 1983). The fitting of the curves (full lines in figure 2) computed using equation (6) to the measured diffusion coefficients results in $\varepsilon_d = 0.46$ eV. The two values of ε_d, unlike those of ε_s, coincide.

In conclusion, we have measured the solubilities and diffusivities of hydrogen and deuterium in hafnium and discussed the ratios k_{Ds}/k_{Hs} and D_D/D_H. The experimental result is explained if we take into account the anharmonicity of the vibration of the hydrogen isotope in hafnium.

Acknowledgment

Appendix

Application of the perturbation theory yields the explicit form of $E_{n_x n_y n_z}$ for the potential expressed by equation (3);

$$E_{n_x n_y n_z} = 2\hbar\omega_x(n_x + \tfrac{1}{2}) + \hbar\omega_z(n_z + \tfrac{1}{2}) - (\alpha^2/8)(\hbar/m\omega_x)^2(1/m\omega_z)$$

$$\times \{[1/(2\omega_x + \omega_z)][n_x^2 + n_y^2 + 4(n_x + n_y + 1)n_z + 3(n_x + n_y) + 4]$$

$$+ [1/(2\omega_x - \omega_z)][-(n_x^2 + n_y^2) + 4(n_x + n_y + 1)n_z + n_x + n_y]$$

$$+ (4/\omega_z)(n_x - n_y)^2\} + \tfrac{3}{2}\beta_x(\hbar/m\omega_x)^2(n_x^2 + n_y^2 + n_x + n_y + 1)$$

$$+ \tfrac{3}{2}\beta_z(\hbar/m\omega_z)^2(n_z^2 + n_z + \tfrac{1}{2}) + \tfrac{1}{4}\beta_{xy}(\hbar/m\omega_x)^2[4n_xn_y + 2(n_x + n_y) + 1]$$

$$+ \tfrac{1}{2}\beta_{yz}(\hbar/m\omega_x)(\hbar/m\omega_z)[2(n_x + n_y)n_z + n_x + n_y + 2n_z + 1].$$

Some of the values of $E_{n_xn_yn_z} - E_{000}$ are given for small n_x, n_y and n_z in the work of Eckert et al (1983).

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