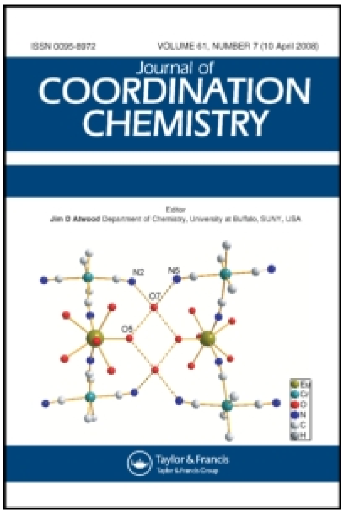

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^{1}H-NMR STUDY OF HYDROGEN INTERCALATED IN β-ZIRCONIUM NITRIDE CHLORIDE

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Hydrogen is taken up by a layer structured compound β-ZrNCl during its chemical vapor transport with NH_4Cl in a sealed silica tube. The transported sample can be further hydrogenated by hydrogen spillover, and dehydrogenated by oxidation with Cl_2 and $KMnO_4$. The infrared absorption spectra indicate that the hydrogen is taken up in the double ZrN layer of β-ZrNCl, coordinating to a nitrogen atom. The second moments of ^{1}H-NMR spectra suggest the formation of hydrogen pairs in β-ZrNCl. A motional line narrowing of the ^{1}H-NMR spectrum was observed at temperatures around 200 K. The activation energy for the jumping motion of the hydrogen was determined to be 10.6 kJ/mol from the temperature dependence of the spin-lattice relaxation time. A possible structural model for the location of hydrogen was proposed.

KEYWORDS: β-zirconium nitride chloride, hydrogen, intercalation, layer structure, ^{1}H-NMR

INTRODUCTION

β-zirconium nitride chloride (β-ZrNCl) is a layer structured compound; the unit layer consists of a double ZrN layer sandwiched between two close-packed chloride layers.[1] Such Cl-Zr-N-N-Zr-Cl layers are stacked with each other by weak van der Waals interactions. Alkali metal atoms and polar solvent molecules can co-intercalate into the van der Waals gap by breaking the weak interactions between the chloride layers,[2–4] On intercalation, the color of β-ZrNCl is changed from pale yellow-green to black due to charge transfer from the alkali metal to the host structure. Since the reaction also occurs electrochemically, applications of β-ZrNCl to cathode materials of a lithium battery and electrochromic devices have been considered.[4]

β-ZrNCl was first synthesized by the reaction of $ZrCl_4$ with NH_3 by Juza and Heners.[5] Ohashi *et al.*[6] developed a new and more efficient synthetic route by the

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direct reaction of ZrH_2 with vaporized NH_4Cl at temperatures about 870 K. The as-prepared sample was purified to highly crystalline β-ZrNCl by chemical vapor transport with NH_4Cl in a sealed silica tube at temperatures from 770 to 1070 K.[7] It was suggested that hydrogen was taken up by β-ZrNCl in the course of the chemical transport.[8] In this study, β-ZrNCl is further hydrogenated by hydrogen spillover and dehydrogenated by oxidation, and the behavior of hydrogen taken up by the structure has been investigated by ^{1}H-NMR measurements.

EXPERIMENTAL

Materials

β-ZrNCl was prepared by the reaction of ZrH_2 with NH_4Cl in a stream of dry NH_3 according to the method described elsewhere.[6] The as-prepared sample was vacuum-sealed with a small amount of NH_4Cl in a fused silica tube, and chemically transported from the lower temperature zone at 1020 K to the higher one at 1120 K in a horizontal furnace. By the chemical vapor transport, β-ZrNCl was purified from oxide contamination and deposited in a highly crystalline form. A certain amount of hydrogen was taken up by β-ZrNCl during the chemical vapor transport.[8]

Further hydrogenation of the as-transported sample was carried out by hydrogen spillover on the sample with platinum deposited as follows: the as-transported sample was soaked in a hydrogen chloroplatinate (H_2PtCl_6) solution in such a way that 0.5 wt% of Pt was deposited to β-ZrNCl by heat-treatment in a stream of H_2 at 423 K. During the treatment, the chloroplatinate was decomposed to Pt metal, which catalyzed the hydrogenation of β-ZrNCl by hydrogen spillover.

The dehydrogenation of the as-transported β-ZrNCl was performed by two kinds of oxidation reactions. The sample was dispersed in chloroform, and refluxed at 338 K for 3 h in a stream of Cl_2 gas. The sample was separated and washed with chloroform after standing in the solution overnight at room temperature. The as-transported β-ZrNCl was also subjected to oxidation with $KMnO_4$. The sample was dispersed in a 0.1 M $KMnO_4$ solution in 0.5 M H_2SO_4, and refluxed at 373 K for 3 h. After cooling down to room temperature, the sample was separated by filtration followed by washing with a $NaHSO_3$ solution in 0.25 M H_2SO_4 to remove the precipitated MnO_2. The separated sample was dried in vacuum at 383 K.

Analyses

The X-ray powder diffraction (XRD) pattern was measured using a Rigaku RAD-B diffractometer. Graphite monochromatized Cu Kα radiation was used. Infrared (IR) spectra were measured by a KBr disk using a Perkin Elmer 1600 FT-IR spectrometer. Electric dc conductivity was measured in a temperature range of 150 K to room temperature by a four-probe method on the powder sample compressed at a pressure of about 100 MPa. ^{1}H-NMR spectra and spin-lattice relaxation times (T_1) were measured using a Bruker AMX-400 spectrometer in a temperature range of 155 to 420 K. T_1 was determined by using the inversion recovery method with the pulse sequence of 180°–τ–90°. The intensity of the inversion recovery signal followed a single exponential curve against τ at all temperatures.

RESULTS

Hydrogenation and Dehydrogenation

The IR spectra of β-ZrNCl measured before and after various treatments are shown in Figure 1. The absorption bands observed at 3130 and 1400 cm^{-1} were assigned to N-H stretching and N-H deformation vibrations, respectively. The frequencies are coincident with those of vibrational modes of NH_4^+ of NH_4Cl. The intensities of the absorption bands increased after hydrogenation by the spillover and decreased after dehydrogenation by oxidation with Cl_2 and $KMnO_4$. This finding suggests that although the frequencies of the absorption bands observed are almost coincident with those of NH_4Cl, the possibility of contamination with NH_4Cl used as a chemical transport agent is excluded.

The hydrogen contents (Table 1) in the as-transported and the treated samples of H_xZrNCl were estimated on the basis of the integrated ^{1}H-NMR spectra with reference to the spectrum of NH_4Cl added as an internal standard. The amounts of hydrogen in the variously treated samples were compared with those estimated from the relative intensities of the N-H vibrational bands of the corresponding IR

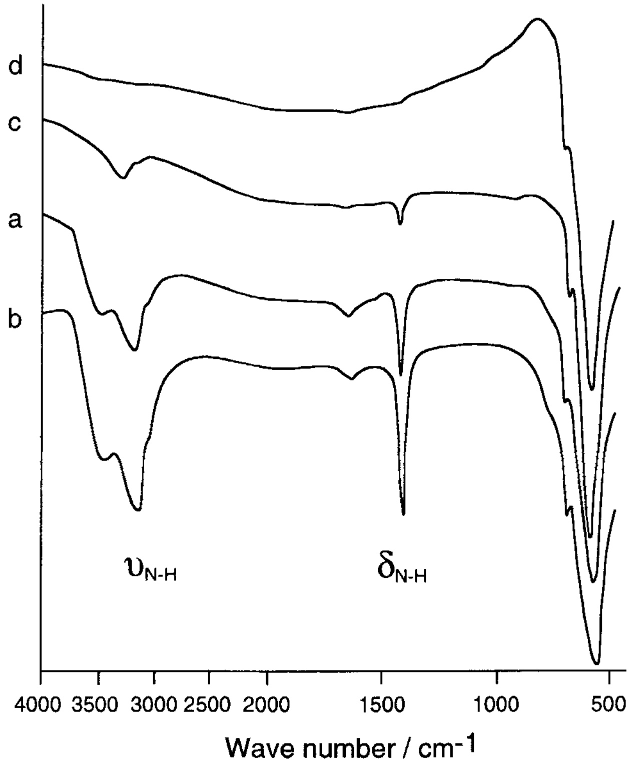

Figure 1 IR specra of the hydrogenated and dehydrogenated β-ZrNCl: (a) as-transported, (b) hydrogenated by spillover, and dehydrogenated by oxidation with (c) Cl_2 and (d) $KMnO_4$.

Table 1 Hydrogen contents in H_xZrNCl determined by ^{1}H-NMR study.

H_xZrNCl	x
As-transported	0.23
Hydrogenated by spillover	0.65
Oxidized with Cl_2	0.09
Oxidized with $KMnO_4$	0.04

spectra, which were found to be in good agreement with each other. The lattice constants of all of the samples were essentially unchanged at $a = 0.3602(2)$ nm and $c = 2.767(1)$ nm.

Electrical conductivities (σ) of the as-transported and dehydrogenated samples were measured in the temperature range 150 to 300 K, and are shown in Figure 2 as a function of reciprocal absolute temperature. H_xZrNCl was a semiconductor with an activation energy of about 50 meV for the conduction at temperatures around 200 K, which was calculated from the slope of plots of log σ *vs.* $1/T$ (solid lines in Fig. 2). As the temperature was raised above 250 K, the conductivity tended to move into a saturation region. The activation energy appeared to be little

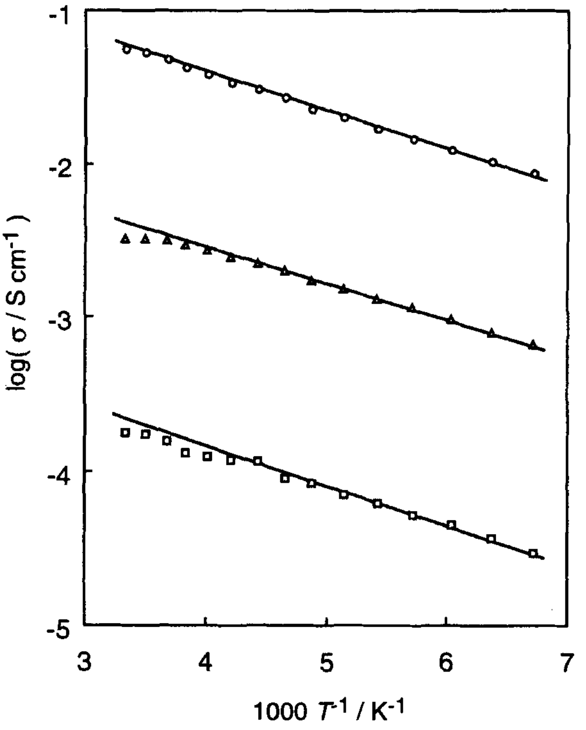

Figure 2 Electrical conductivity of H_xZrNCl; as-transported (○) and dehydrogenated by the oxidation with Cl_2 (△) and $KMnO_4$ (□).

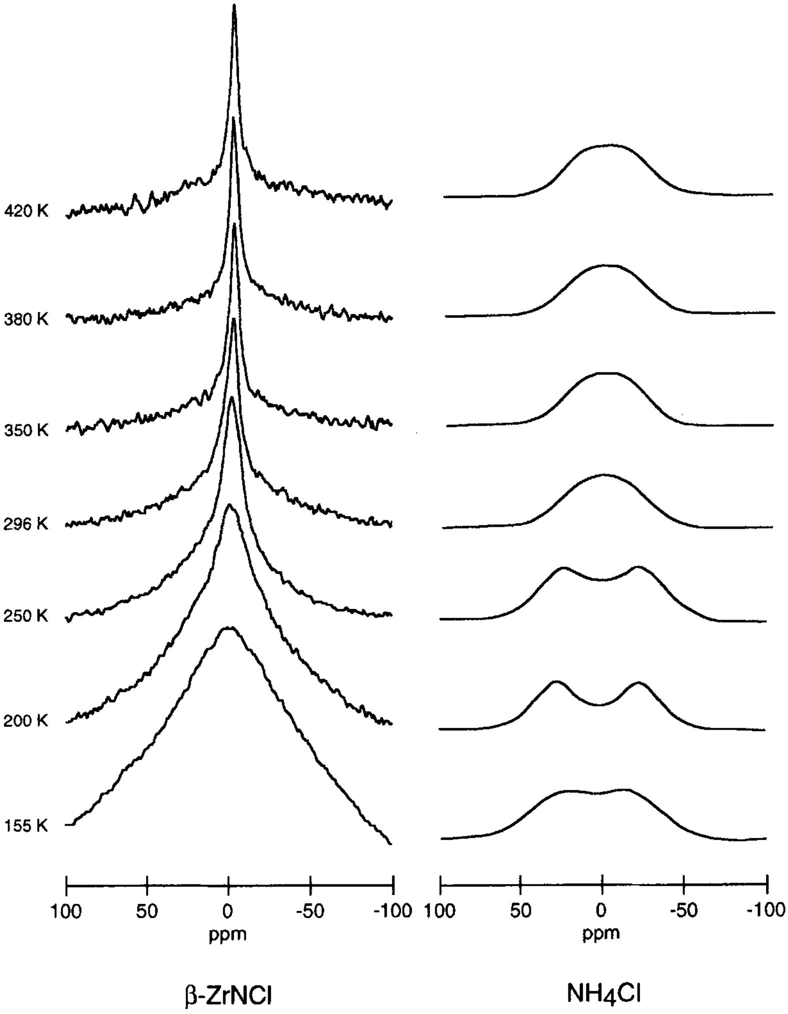

Figure 3 ^{1}H-NMR spectra of as-transported H_xZrNCl and NH_4Cl measured at different temperatures.

affected by the amount of hydrogen, although the electrical conductivity of H_xZrNCl decreased remarkably with reduction of hydrogen content.

The β-ZrNCl is a pale yellow-green crystal with an optical band gap of 3.2 eV which is much larger than the activation energy for the conduction.[9] The H_xZrNCl is an n-type semiconductor[8] and the color was essentially unchanged by hydrogenation and dehydrogenation. This suggests that the high electrical conductivity in H_xZrNCl is due to ionization of the donor impurities formed at a level of about 50 meV below the conduction band. The saturation of conductivity is due to the complete ionization of the shallow donor levels. It is very likely that the donor levels are made by uptake of hydrogen atoms. The low electrical conductivity of the dehydrogenated sample can be interpreted in terms of the low concentration of the donors.

^{1}H-NMR spectra

The ^{1}H-NMR spectra of the as-transported sample of β-ZrNCl were measured in a temperature range of 155 K to 420 K, and are shown in Figure 3 in comparison with those of NH_4Cl measured at the same temperatures. H_xZrNCl shows a single resonance, while NH_4Cl has a profile characteristic of the tetrahedral $NH_4{}^+$ group. The line width for H_xZrNCl at 296 K was about 13 ppm, which is much sharper than 60 ppm for NH_4Cl crystal. However, as can be seen from Figure 3, the former line width became broader than that of NH_4Cl below 155 K. The second-moments (M_2) of the resonance lines of H_xZrNCl shown in Figure 3 were calculated, and are given in Figure 4 as a function of temperature. A motional line narrowing, *i.e.*, a rapid drop of M_2, was clearly observed at temperatures around 200 K. Above 350 K, the M_2 was independent of temperature. The M_2 value can be extrapolated to a value of about 0.5 mT^2 at 0 K, which corresponds to the limitation of a rigid-lattice model when hydrogen motion becomes sufficiently slow. The M_2 value can be related to the arrangement of hydrogen atoms in the host lattice. The position of the hydrogen atom in β-ZrNCl was estimated by comparing the M_2

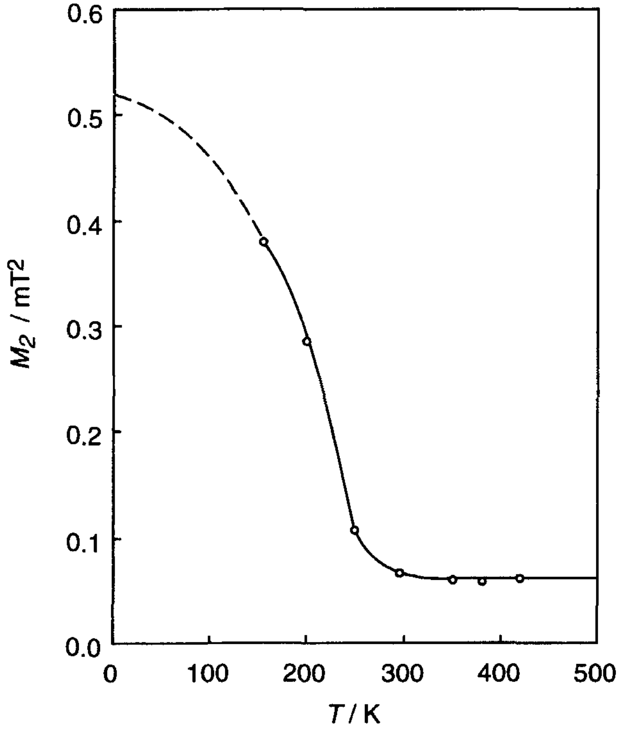

Figure 4 The temperature dependence of the second-moment of ^{1}H-NMR spectra of as-transported H_xZrNCl.

values calculated on the basis of possible arrangements of hydrogen atoms by the Van Vlech formula.[10]

The appearance of the N-H vibration bands in the IR spectra of hydrogenated β-ZrNCl (Figure 1) suggests that the hydrogen atoms should be located near the nitrogen atoms of β-ZrNCl. It was assumed that the hydrogen was taken up in the trigonal interstices of the double ZrN layer as shown in Figure 5, where the hydrogen is coordinated by three zirconium atoms and a nitrogen atom. The M_2 value calculated for the hydrogen (H_I) is 0.005 mT^2, which is much smaller than the observed value of 0.5 mT^2. The M_2 value for the hydrogen (H_{II}) between the chloride layers is 0.003 mT^2, which is also much smaller. The M_2 value is predominantly determined by the dipole-dipole interaction between the nearest hydrogen atoms. It appears to be impossible to realize such a large M_2 value without considering a pair of hydrogen atoms in the structure.

Spin-Lattice Relaxation Time of ^{1}H-NMR

The temperature dependence of the spin-lattice relaxation time T_1 measured over a temperature range of 180 to 360 K is shown in Figure 6 as a function of reciprocal

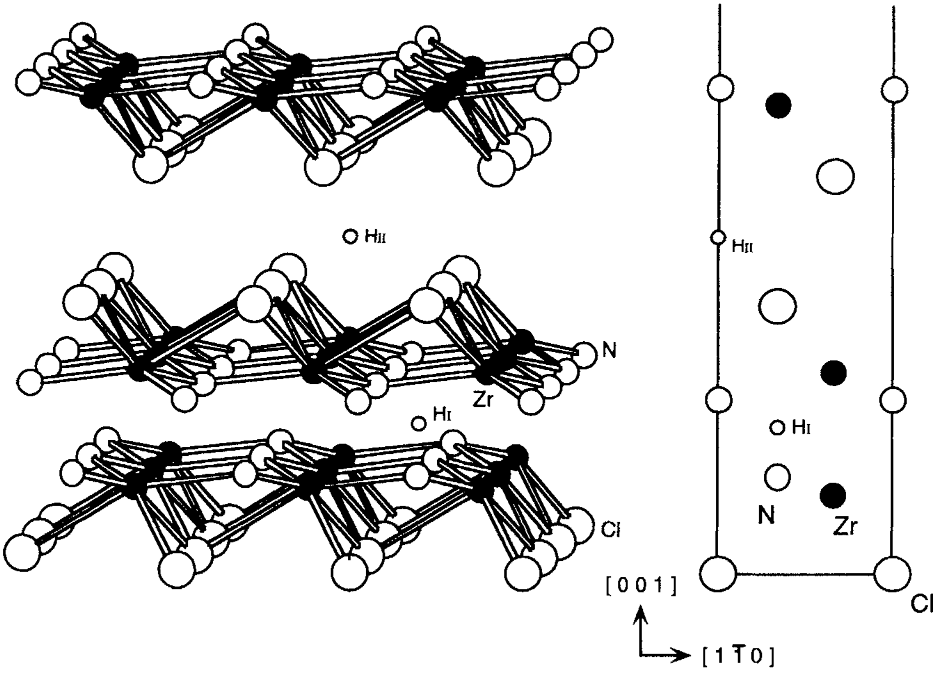

Figure 5 Structure of β-ZrNCl and possible hydrogen sites H_I and H_{II}: (a) perspective view and (b) (110) projection.

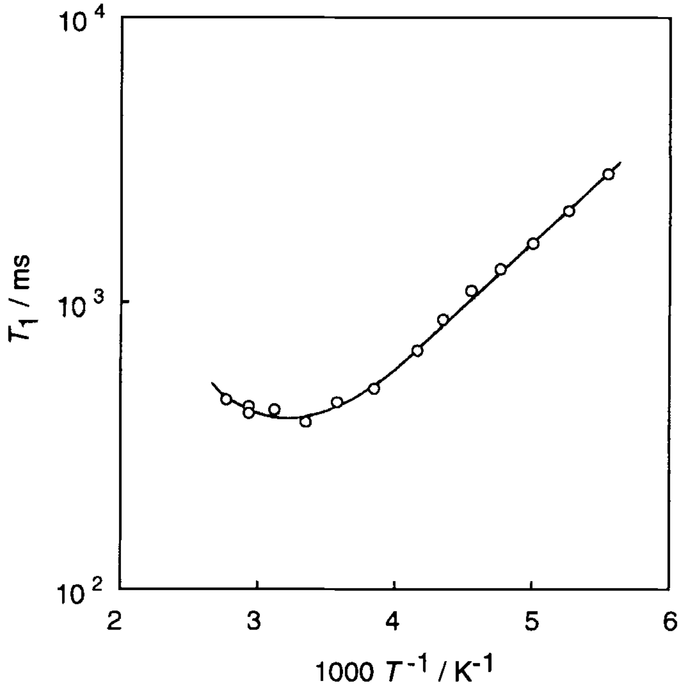

Figure 6 Temperature dependence of T_1 for as-transported H_xZrNCl.

absolute temperature. It exhibits a v-shaped behavior expected from a relaxation dominated by diffusional motion. The jump frequencies for the motion are obtained from T_1 using the Bloembergen-Purcell-Pound (BPP) theory[11–13] by ignoring contributions of the conduction-electron and paramagnetic impurity. The BPP theory gives us:

$$T_1^{-1} = \frac{(T_1^{\mathrm{m}})^{-1}}{F_{\mathrm{m}}}\left[\frac{\omega\tau}{1+\omega^2\tau^2}+\frac{4\omega\tau}{1+4\omega^2\tau^2}\right]$$

where τ is the correlation time, ω is the angular resonance frequency, F_{m} is the maximum value of the function in the large parentheses, and T_1^{m} is the minimum value of T_1.[11] The minimum in T_1 occurs at the temperature when the jump frequency is the same order as the resonance frequency. The logarithm of correlation time, which is the reciprocal of the jump frequency, is shown in Figure 7 as a function of reciprocal absolute temperature. The activation energy and the preexponential factor τ_0 are determined to be 10.6 kJ/mol and 1.9×10^{-11} sec, respectively from the straight line of the Arrhenius equation. It is reasonable to consider that the jumping occurs between the nearest sites in the double ZrN layer. It should be noted that the hydrogen atoms move extremely rapidly in the β-ZrNCl crystal.

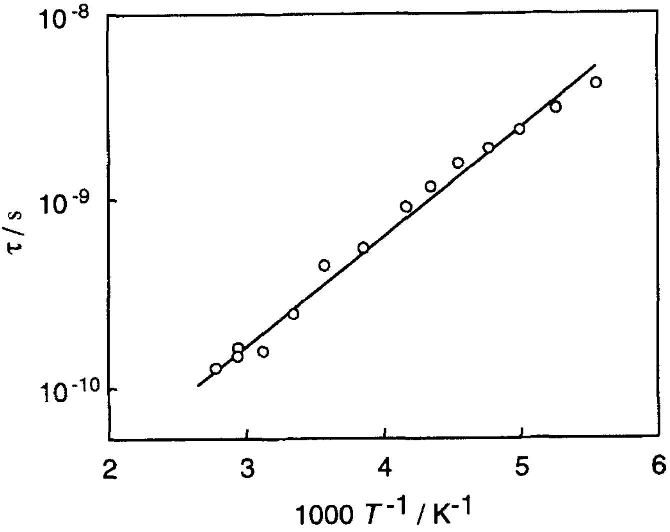

Figure 7 The correlation time (τ) of the jumping motion of hydrogen as a function of reciprocal temperature for as-transported H_xZrNCl.

DISCUSSION

It is interesting to note the resemblance between the structures of zirconium monohalides ZrX (X = Cl, Br)[14,15] and β-ZrNCl. As shown in Figure 8, both of the structures consist of double zirconium metal layers sandwiched by two close-packed chloride or (bromide) layers, and such layers sequenced X-Zr-Zr-X (X = Cl, Br) are stacked with each other by van der Waals interactions. In β-ZrNCl, the double zirconium metal layers from trigonal prismatic interstices and a nitrogen atom occupies each interstice as shown in Figure 8 (b). In ZrCl or ZrBr, the double metal

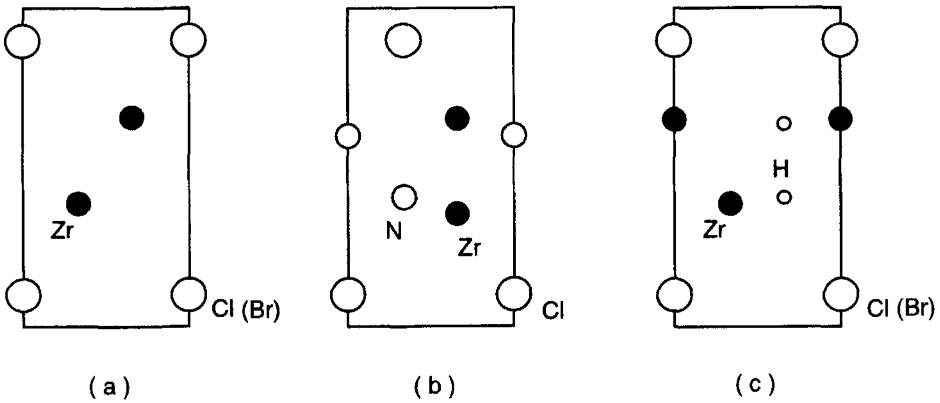

Figure 8 (110) projections of the structures of the unit layers of (a) ZrCl(Br), (b) β-ZrNCl and (c) ZrXH (X = Cl, Br).

layers provide trigonal antiprismatic interstices which are occupied by hydrogen pairs in the formation of monohydride ZrXH (X = Cl, Br) as shown in Figure 8(c).[16]

Although it is very likely that the hydrogen atoms taken up by β-ZrNCl are located near the nitrogen atoms between the zirconium layers as proposed in a previous study,[8] the large second moment value obtained by the ^{1}H-NMR study suggested the presence of a strong dipole-dipole interaction, or formation of hydrogen pairs. As in the formation of monohydrides of zirconium monohalides (Figure 9(a)),[16] it may also be possible that the hydrogen atoms are bound to nitrogen atoms as pairs. However, since the zirconium metal trigonal interstices are already occupied in half by nitrogen atoms, and the distance between the nearest nitrogen atom sites is as short as 0.21 nm, the hydrogen pairs would be located between the nitrogen atoms as shown in Figure 9(b).

It is well known that some transition metal oxides such as WO_3, MoO_3 and V_2O_5 form oxide bronzes with hydrogen as well as lithium.[17,18] The electrons donated from the lithium and the hydrogen are delocalized through the crystals, and give rise to drastic changes in the optical and the electrical properties of the crystals. The changes in physical properties are mainly dependent on the concentration of electron carriers, but not on the kind of the electron donor, lithium or hydrogen. In the case of β-ZrNCl, lithium is intercalated between the chloride layers[19] and brings about the changes in the physical properties of the crystal in a manner similar to hydrogen and lithium in transition metal oxides; the color of β-ZrNCl changes from pale yellow-green to black and the electrical conductivity increases by several orders of magnitude. It is interesting to note, however, that the hydrogen taken up by the double ZrN layers did not give rise to color change. The difference in the action of hydrogen in the formation of bronzes with transition metal oxides and β-ZrNCl can be interpreted in terms of the difference in the interaction with the interlayer surfaces; the hydrogen atoms are located in a ZrN double layer and bound by nitrogen atoms with a covalent interaction. The electrons from the hydrogen atoms appear to be rather localized near the N-H bonds, forming shallow donor levels below the conduction band.

Various kinds of metal hydrides[20,21] and hydrogen-containing bronzes,[22,23] have been studied by solid state ^{1}H-NMR. The activation energy determined in this study for the motion of hydrogen in β-ZrNCl is 10.6 kJ/mol, which is smaller than those of H_xWO_3 bronze (12.7 kJ/mol)[22] and zirconium hydride ZrH_x ($1.58 < x < 1.69$: 13.4 kJ/mol; $x = 1.96$: 14.7 kJ/mol).[21] Because of the low activation energy of the jumping motion for hydrogen in β-ZrNCl, it may be possible for β-ZrNCl to

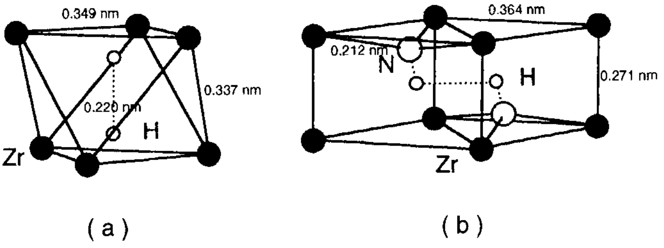

Figure 9 Hydrogen pairs in the interstices of double Zr layers: (a) ZrXH (X = Cl, Br) and (b) H_xZrNCl.

become a good mixed conductor for protons and electrons, which will be useful for cathode materials of hydrogen batteries and hydrogen reversible electrodes.

Acknowledgement

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References

1. R. Juza and H. Friedrichsen, *Z. Anorg. Allg. Chem.*, **332**, 173 (1964).
2. S. Yamanaka, M. Ohashi, S. Sumihara and M. Hattori, *Chem. Lett.*, 1403 (1984).
3. M. Ohashi, S. Yamanaka, S. Sumihara and M. Hattori, *J. Inclusion Phenomena,* **2**, 289 (1984).
4. M. Ohashi, T. Shigeta, S. Yamanaka and M. Hattori, *J. Electochem. Soc.*, **136**, 1806 (1989).
5. R. Juza and J. Heners, *Z. Anorg. Allg. Chem.*, **332**, 159 (1964).
6. M. Ohashi, S. Yamanaka, M. Sumihara and M. Hattori, *J. Solid. State Chem.*, **75**, 99 (1988).
7. M. Ohashi, S. Yamanaka and M. Hattori, J. *Solid. State Chem.*, **77**, 342 (1988).
8. M. Ohashi, H. Nakano, S. Yamanaka and M. Hattori, *Solid State Ionics,* **32/33**, 97 (1989).
9. M. Ohashi, S. Mizoguchi, S. Yamanaka and M. Hattori, *Nippon Kagakukaishi,* 1924 (1987).
10. J.H. Van Vleck, *Phys. Rev.*, **74**, 1168 (1948).
11. N. Bloembergen, E.M. Purcell and R.V. Pound, *Phys. Rev.*, **73**, 679 (1948).
12. W.A. Barton and C.A. Sholl, *J. Phys.*, **C13**, 2579 (1980).
13. L.D. Bustard, *Phys. Rev.* **B22**, 1 (1980).
14. D.G. Adolphson and J.D. Corbett, *Inorg. Chem.*, **15**, 1820 (1976).
15. R.L. Daake and J.D. Corbett, *Inorg. Chem.*, **16**, 2029 (1977).
16. S.D. Wijcyesekcra and J.D. Corbctt, *Solid State Commun.*, **54**, 657 (1985).
17. P.G. Dickens and M.F. Pye, "Intercalation Chemistry" (M.S. Whittingham and A.J. Jacobson, Ed., Academic Press, New York, 1982), pp. 539.
18. M. Greenblatt, *Chem. Rev.*, **88**, 31 (1988).
19. M. Ohashi, K. Uyeoka, S. Yamanaka and M. Hattori, *Bull. Chem. Soc., Jpn.*, **64**, 2814 (1991).
20. R.C. Bowman, Jr, E.L. Venturini and W.K. Rhim, *Phys. Rev.*, **B26**, 2652 (1982).
21. C. Korn and S.D. Goren, *Phys. Rev.* **B33**, 68 (1986).
22. K. Nishimura, *Solid State Commun,* **20**, 523 (1976).
23. D.A. Claridge, P.G. Dickens and J.B. Goodenough, *Appl. Phys.*, **A49**, 65 (1989).