

## HYDROGEN IN $\beta$ -ZrNCI

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### ABSTRACT

Position and content of hydrogen atoms in as-transported  $H_xZrNCI$ , which is the parent compound of a novel two-dimensional superconductor  $Li_{0.16}ZrNCI$  with  $T_c=15K$ , are determined by powder neutron diffraction. Hydrogen atoms are found to occupy 6c site with  $z=0.235$ , which is located between ZrN layer and Cl layer, and with an occupancy,  $g=0.4$ , *i.e.*,  $x=0.4$ .

Keywords: A. inorganic compounds, B. chemical synthesis, C. neutron scattering, D. crystal structure

$\beta$ -ZrNCl is a parent compound of novel layered superconductor  $\text{Li}_x\text{ZrNCl}$  with  $T_c \leq 15\text{K}$ , which has been discovered by Yamanaka et al. [1]. The structure of  $\beta$ -ZrNCl is SmSI type ( $R\bar{3}m$ ) [2], which is made of the ordered stacking of Zr, N, and Cl triangular lattice planes with the sequence of [Cl-Zr-N-N-Zr-Cl].  $\text{Li}_x\text{ZrNCl}$  is known to contain hydrogen atoms, conceivably due to the sample preparation procedure with  $\text{NH}_3$  gas [1]. Although the hydrogen does not affect the superconductivity appreciably, infrared spectra show the existence of the N-H bond, which has the similar frequency ( $1400\text{cm}^{-1}$  and  $3100\text{cm}^{-1}$ ) to that of  $\text{NH}_4^+$  [3]. It would be interesting to study how these hydrogen atoms can be observed at  $T=4\text{K}$  by neutron diffraction measurement.

$\beta$ -ZrNCl was prepared by the reaction of  $\text{ZrH}_2$  (99.7%) with  $\text{NH}_4\text{Cl}$  (99.5%) at  $650^\circ\text{C}$  for 30min under the flow of  $\text{NH}_3$  gas (99.9%, 20-50cc/min). Obtained  $\beta$ -ZrNCl sample was purified by a chemical vapor transport as described in the literature [3]. The purified  $\beta$ -ZrNCl still contains hydrogen atoms. For comparison, some of  $\beta$ -ZrNCl sample was dehydrogenated by oxidation with  $\text{KMnO}_4$  [3]. The content of hydrogen in this dehydrogenated sample was estimated to be 0.04 [3]. Since the value, 0.04, is much smaller than the hydrogen content in as-transported  $\text{H}_x\text{ZrNCl}$ , e.g., 0.23 in Ref. 4, the hydrogen in dehydrogenated  $\beta$ -ZrNCl is neglected in the present analyses. The samples with the weight of 3.79g and 3.78g were sealed in Al cans filled with He gas for dehydrogenated  $\beta$ -ZrNCl (ZrNCl) and as-transported  $\text{H}_x\text{ZrNCl}$  ( $\text{H}_x\text{ZrNCl}$ ), respectively, resulting in almost the same packing density. Neutron diffraction measurements were carried out using two-axis spectrometer HERMES at T1-3 thermal guide of JAERI-JRR3M in

Tokai. The wave length of incident neutron was 1.8196Å. The diffraction intensity was collected from 5° to 154.9° in  $2\theta$  by 150 counters stepped by 0.1°. The results obtained by neutron diffraction were refined using the Rietveld analysis computer program RIETAN [4].

Fig. 1 shows observed diffraction intensity of  $H_xZrNCl$ , and intensity difference where we subtracted the intensity of  $ZrNCl$  from that of  $H_xZrNCl$  in the same scale of monitor counts (1440kcps~24min). The most prominent difference can be seen at the highest 110 reflection, while there were no peaks that can change the space symmetry,  $R\bar{3}m$ . If we assume hydrogen atoms sit on 3a, 3b, or 6c site, the 110 peak intensity increases proportional to the square of the sum of all atoms' scattering length times its occupancy. In that case, 110 peak intensity would decrease, since only a hydrogen atom has a negative scattering length. On the other hand, if hydrogen atoms occupied 9e or 9d site, 110 peak intensity would increase. The large reduction of 110 peak intensity (12.46(4)% of that in  $H_xZrNCl$ ) in Fig. 1 indicates that hydrogen atoms occupy 3a, 3b, or 6c sites with  $x=0.40$ , which is higher than  $x=0.19$  reported in Ref. 4. If hydrogen atoms sit at other 36i, 18h, 18g, or 18f site in  $R\bar{3}m$  with the same occupancy, the hydrogen content must exceed the  $x=0.40$  level. Such a large value is unreasonable in comparison with that reported in Ref. 4. Once we determine that the hydrogen content in  $H_xZrNCl$  is 0.4, other differences of peak intensities have an information about the hydrogen z position, unless other atoms move significantly by the introduction of hydrogen atoms. Since we have not observed any structural phase transition, it is reasonable to assume that the change in the positional parameters due to the hydrogenation would be small. As shown in Fig. 1, 003 peak intensity increased by

5.91(3)% for  $H_xZrNCl$ , while 0015 peak intensity decreased by 3.1(1)%. Based on these changes, we estimated the position,  $z$ , of hydrogen at 6c site to be about 0.08 or 0.24. The former site is far from N position, while the latter site is coordinated by one N atom and three Cl atoms. Since IR spectra show only N-H vibrations that coincide in energy with those of  $NH_4^+$  of  $NH_4Cl$  [3], the hydrogen would be coordinated by a nitrogen atom with the bond length of 1.015Å as in  $NH_4^+$ . Based on all these conditions, most reasonable site of hydrogen atoms is determined at 6c site with  $z \sim 0.24$ . Rietveld analysis was performed using this hydrogen position as an initial parameter with keeping the bond length (1.015Å) between N and H atoms, where the occupation factor and the thermal parameter of a hydrogen site were fixed to be 0.4 and the same thermal parameter with a N site, respectively. Fig. 2 shows an observed, calculated, and difference plots for the refinement of  $H_xZrNCl$  at  $T=4K$ . The refined parameters are listed in Table. The Zr, N and Cl occupation factors were fixed at unity in the present analysis, as the stoichiometry is confirmed by a chemical analysis of  $\beta$ -ZrNCl (Zr:N:Cl=1:1:1) [5]. The large thermal parameters similar to those of ZrNCl [2] may be due to the stacking faults along the c-axis. Previous assumption in Ref. 4, where the hydrogen atoms are located at around 3b site, is excluded in the present report, since it leads to an inconsistent decrease of 003 peak intensity.

Fig. 3 shows the difference of neutron diffraction background intensities between  $H_xZrNCl$  and ZrNCl at 4K. The difference is expected to come from only incoherent scattering by additional hydrogen atoms in  $H_xZrNCl$ . Q-dependence of the intensity difference indicates an isotropic vibrational parameter,  $B_{eq}$ , of

hydrogen atoms at 4K is  $1.27(3)\text{\AA}^2$ . The hydrogen content of  $\text{H}_x\text{ZrNCl}$  was estimated to be 0.43 from this incoherent scattering intensity (239(2) counts/24min at  $Q\sim 0$ ), having reasonable agreement with the value 0.40 estimated from 110 peak intensity.

Fig. 4 shows the structure of  $\text{H}_x\text{ZrNCl}$  determined by the present neutron diffraction. Since the hydrogen position is outside of the ZrN honeycomb bilayer, where an electronic conduction is expected in superconducting  $\text{Li}_x\text{ZrNCl}$ , these hydrogen atoms may not affect the superconductivity appreciably. However, minute change of a critical temperature by an isotope effect or the change of charge can be expected.

In conclusion, we have studied the hydrogen position and content in as-transported  $\text{H}_x\text{ZrNCl}$  by powder neutron diffraction. Although it was difficult to determine them because of its little occupation and small scattering length compared with those of other atoms, an analysis of the difference between the intensities of as-transported  $\text{H}_x\text{ZrNCl}$  and dehydrogenated  $\text{ZrNCl}$  enabled us to conclude that hydrogen atoms sit on 6c site with  $z=0.235$  and with an occupancy  $g$  (or  $x$ )=0.4. This result indicates that hydrogen atoms outside of an electronic conducting plane (ZrN) may not affect the superconductivity in  $\text{Li}_x\text{ZrNCl}$  appreciably.

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## Table

Table Structural parameters of  $H_xZrNCl$  at  $T=4K$

$$R\bar{3}m; a=3.5981(2) \text{ \AA}, c=27.555(2) \text{ \AA}$$

atom	site	<i>g</i>	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}/\text{\AA}^2$
Zr	6c	1.0	0	0	0.1211(1)	4(1)
N	6c	1.0	0	0	0.1981(1)	5(5)
Cl	6c	1.0	0	0	0.3870(1)	4(2)
H	6c	0.4	0	0	0.2349	5

$$R_1=2.31\%, R_p=7.27\%, R_{wp}=9.59\%, R_e=3.53\%$$

## Figure Captions

Fig. 1 Observed profile of  $H_xZrNCl$  and the difference profile from that of  $ZrNCl$  at  $T=4K$ .

Fig. 2 Observed, calculated, and difference profiles for  $H_xZrNCl$  at  $T=4K$ .

Fig. 3 Difference in the backgrounds between  $ZrNCl$  and  $H_xZrNCl$  diffraction intensities at  $T=4K$ . Solid line shows Debye-Waller factor,  $e^{-2W}$ , with  $B=1.27\text{\AA}^2$ .

Fig. 4 Structure of  $H_xZrNCl$  determined by the present neutron diffraction.

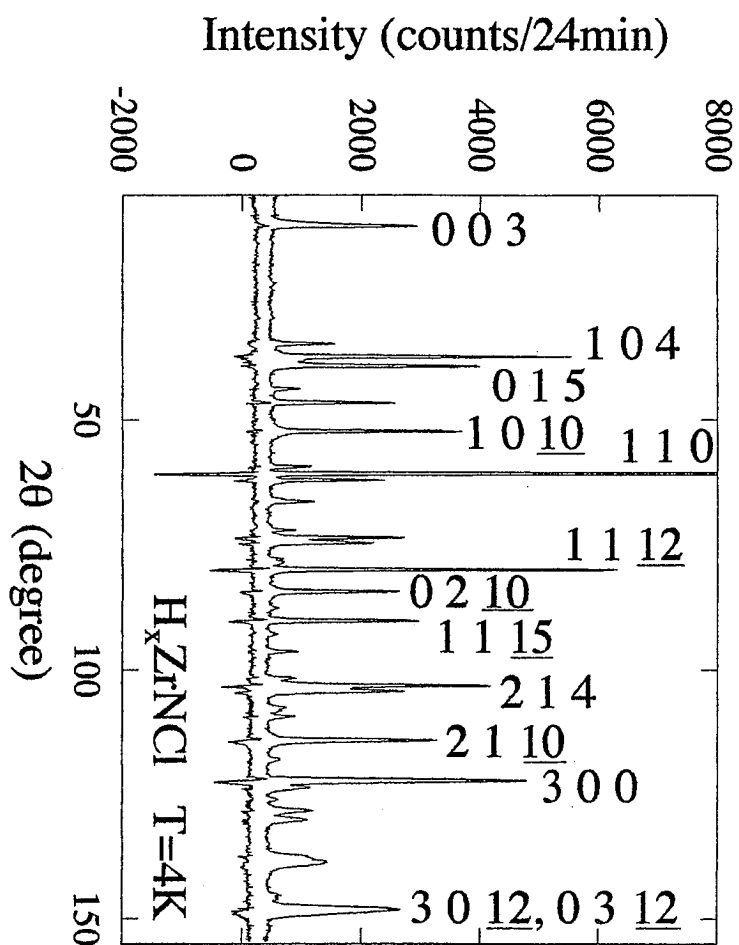


Fig. 1 Shamoto et al.

$126 \times 10 \text{ cm}^2$

$595 \text{ cm} \approx 15.5 \text{ \AA}$



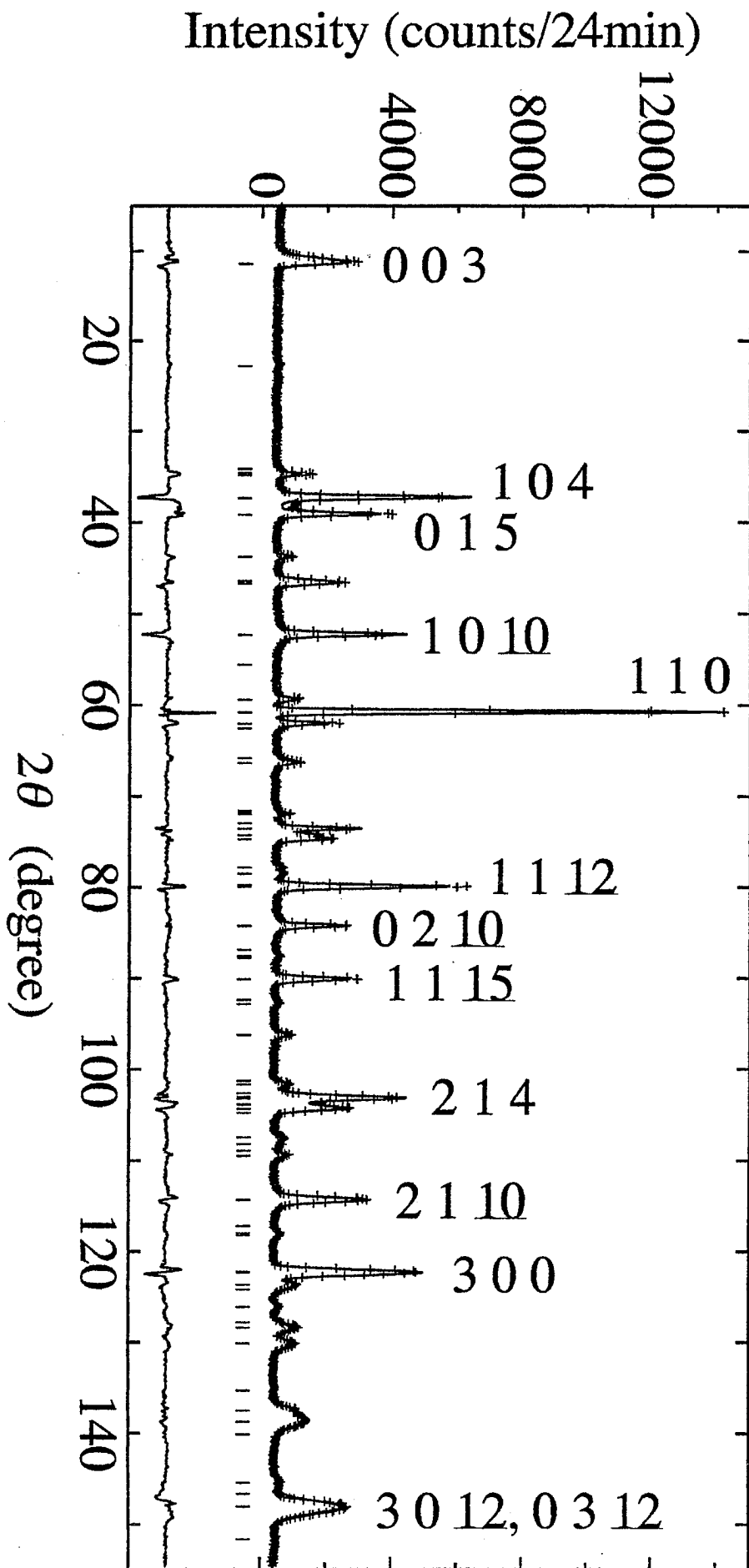


Fig. 2 Shamoto et al.

25.5 X 12.2  
3.59<sub>001</sub> = 9.35 Å

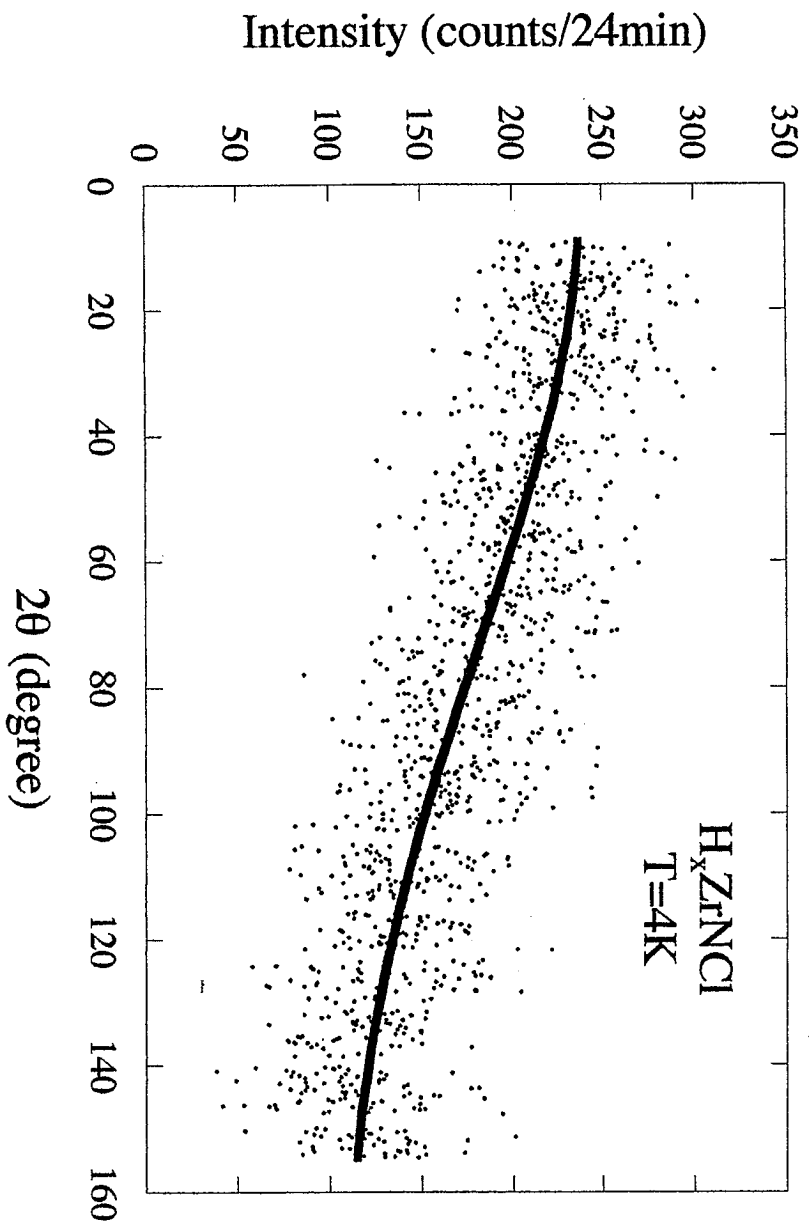


Fig. 3 Shamoto et al.

16 × 11 cm<sup>2</sup>  
5.2 cm ≅ 13.4 Å

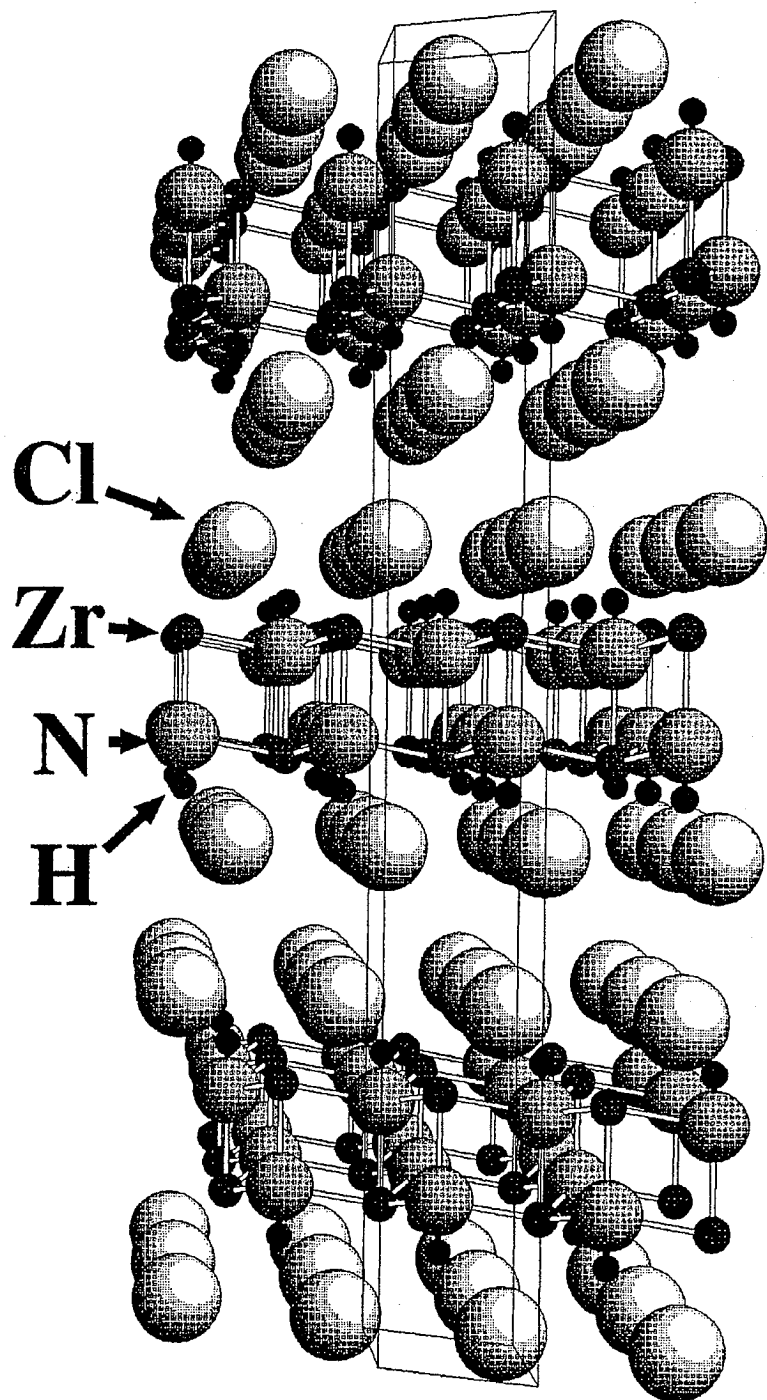


Fig. 4 Shamoto et al.

$10.7 \times 17 \text{ \AA}$

$13.7 \text{ \AA} \equiv 35.6 \text{ \AA}$   
 $\rightarrow 21.4 \text{ \AA}$

±5% × 60% 縮小