A High Pressure Apparatus for Neutron Diffraction*

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Synopsis

A high pressure apparatus was developed for thermal neutron diffraction of time-of-flight method. The high pressure vessel was a piston-cylinder type, and Ti-Zr alloy was used as a material of the cylinder. The coherent scattering of neutron is suppressed in Ti-53wt% Zr alloy. The diffraction spectrum is formed of peaks from the specimen and a background, which corresponds to the energy distribution of the incident neutron.

High pressure measurements were made in RbBr on the transformation between NaCl-type structure and CsCl-type to a pressure about 20 kb, and a good agreement was confirmed with former experiments.

I. Introduction

The diffraction of thermal neutron from materials under pressure is one of the important methods to obtain informations on the atomic level.[1] The informations on the atomic arrangement are the distance between atomic planes, distribution of atoms and the symmetry of the atomic position. The compressibility of the material and the structural transformation under pressure are deduced directly from the experiments. In the case of neutron diffraction, the atomic scattering and absorption of neutron beam has no regular relation with atomic number in contrast with the case of X-ray. This gives us a chance to study lighter elements and gives a freedom in the selection of materials for the high pressure apparatus.

Under the atmospheric pressure, the diffractometry has been established and the highly accurate methods or the simple and reliable technics are developed already. We are expecting to develop technics

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of diffraction under pressure to the accuracy in the same order with in atmospheric pressure. However, in the case of high pressure, the specimens are surrounded by materials for generating pressure and by pressure-transmitting medium. Both materials absorb the radiation, contribute additional diffraction not wanted, and act to reduce the accuracy of measurements.

So the thinner wall thickness is desirable for the apparatus designed for the high pressure work. In the case of the time-of-flight (TOF) method of neutron diffraction, the diffraction angle is fixed and the energy distribution of the scattered beam is analyzed. Hence the thin slits are cut on the pressure vessel for the intake of neutron beam and for the outlet of diffraction beam, and the lowering of strength of the vessel could be minimized. This is an advantage to use TOF method for the high pressure measurements.

The coherent scattering amplitude of thermal neutron wave takes plus or minus signs depending on elements. In some combinations of elements in alloys or compounds, we have a possibility to obtain materials without coherent scattering. If such materials are strong enough to keep the pressure, the difficulty of additional scattering could be dissolved. A combination of Ti-Zr is one of these materials.[2)]

For the neutron diffraction under pressure, some methods are reported: utilization of Ti-Zr alloy as a vessel for the angular scanning of monochrematized beam[3)], or the use of alumina cell reinforced by steel ring for TOF method using the material testing reactor as a neutron source.[4)]

In this report, descriptions will be given on the high pressure apparatus made of Ti-Zr alloy for the TOF neutron diffraction and on some preliminary works. In the present study we utilize the facilities of TOF neutron measurements[5)] installed in the Nuclear Science Laboratory of Tohoku University, composed of a thermal neutron source excited by 300 Mev electron linear accelerator and a data aquisition system controlled by OKITAC 4500 computor.

II. High pressure apparatus

The size of the neutron flux radiated from the source is about 40 x 40 mm^2. In the case of horizontal dispersion, the thin flux extended to the vertical direction is preferable to attain the angular resolution. Hence the specimen must be a thin rod with vertical axis. And the high pressure vessel is a piston-cylinder type with vertical compression.

As material for the pressure vessel, Ti-Zr alloy was selected.

For thermal neutrons about 1 Å in wavelength, the coherent scattering amplitudes are -3.3×10^{-13} cm for Ti and $+6.31 \times 10^{-13}$ cm for Zr. The scattering amplitude of Ti-Zr system is shown in Fig. 1, and the amplitude is zero for 53 wt% (37 at%) Zr. At 50 wt% Zr the amplitude is only 0.4×10^{-13} cm and about one tenth of pure Ti, and the melting and casting of the alloy is not so delicate.

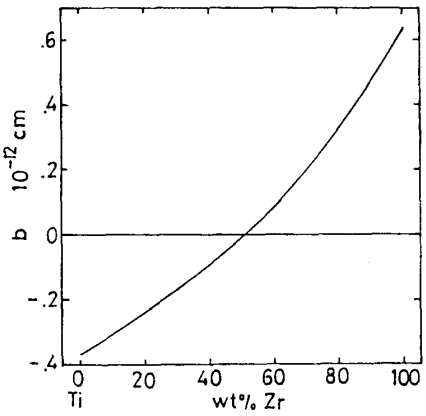

Fig. 1. Coherent scattering amplitude in Ti-Zr system for thermal neutrons.

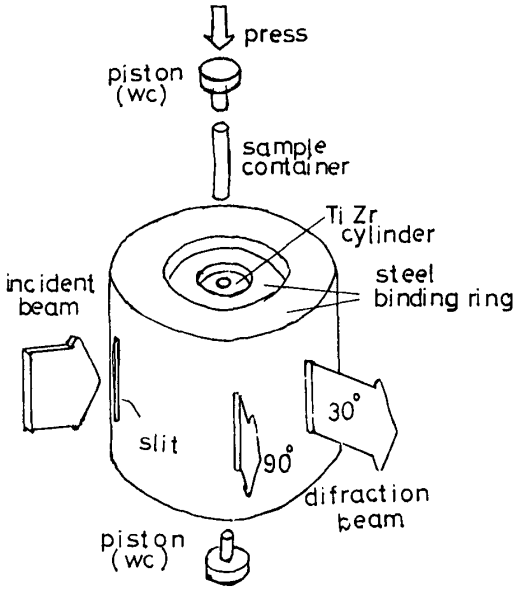

Fig. 2. High pressure apparatus for TOF neutron diffraction.

Sponge Ti and Zr of 99.9% pure are used as raw materials and arc-melted in high pure argon gas. The melting was done in two stages, at first small blocks of the alloy was casted, then the blocks were casted in one ingot, the size of ingots were about 3 to 4 cm diameter and 10 to 13 cm high. Internal defects were tested by radiation photography, no fatal defect was observed in all ingots. The ingots were formed by lathe supplying sufficient amount of coolant, outer surface of the cylinder was polished, inner holes were 7 to 8 mm diameter. The sample container made of teflon 0.2 mm thick was inserted in the hole.

The double binding rings were made of Ni-Cr-Mo steel, the outer diameter of which was 12 cm and the hight was 10 or 12 cm. Slits were cut in both rings and the diffraction angles were set at 30°, 45°, 60° and 90°. Ti-Zr cylinder was shrunk at the inside of the ring. The general view of the high pressure apparatus is shown in Fig. 2. The width of slits were about 5 to 7 mm at the outside, 4 to 5 mm at the inside and the hight was 4 to 5 cm outside and 3.5 to 4 cm inside.

The pistons were made of hardened steel, sintered alumina or tungsten carbide.

The vessel was set in the hydraulic press with a capacity of 50 tons and all are set on the table of the diffractometer. The hydraulic pressure was observed by a bourdon gauge. The aimed value of pressure is 25 kilobar and this value will be reasonable for piston-cylinder type apparatus.

The absorption coefficient of thermal neutron in Ti-Zr alloy is shown in Fig. 3, the absorption in 53 wt% Zr alloy is 0.105 cm^{-1}, the value is situated at lower middle in various materials.

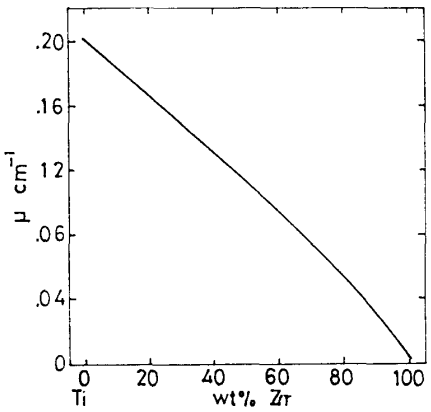

Fig. 3. Absorption coefficient of Ti-Zr system for thermal neutrons.

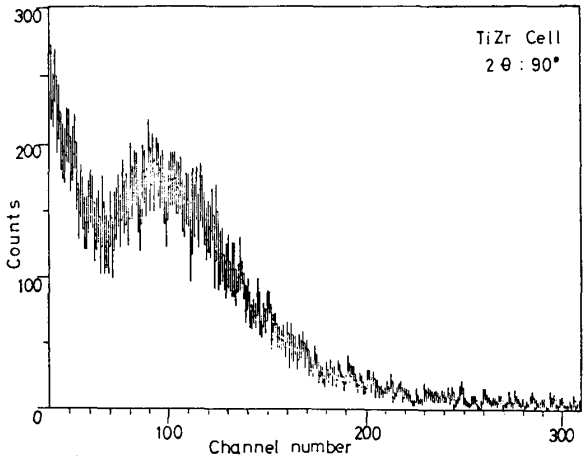

Fig. 4. Sprctrum of neutrons scattered by Ti-Zr cell.

III. Neutron diffraction in Ti-Zr alloy cell

In Ti-53 wt% Zr alloy, the coherent scattering amplitude is zero but the incoherent scattering amplitude is finite. The former gives the diffraction patterns for the hexagonal lattice and the latter gives the scattering proportional to the energy distribution of the incident beam. In Fig. 4, a TOF pattern is shown for the Ti-Zr cell only. In the figure, channel number represents the time-of-flight, energy or the wavelength of the diffracted beam. At the angle of 60°, one hundredth of the channel number nearly equals to the interplanner spacing measured in angstrom unit. The pattern for Ti-Zr is similar to that of vanadium, the roughness of the curve is not due to any kind of ordering in the alloy but due to statistics, because the number of count is small and emphasized by error bars written by the system program.

The patterns for the cell and specimen set at the center of the hole are shown in Figs 5 and 6 for polycrystalline aluminum and iron, respectively. Here, aluminum is selected as a material with moderate scattering amplitude of 3.45×10^{-13} cm and iron as high amplitude of 9.51×10^{-13} cm. In the case of iron, the intensity of each peak is high enough and separated well from the background. In aluminum the peaks are poor in intensity but satisfactory for the mathematical manipulation in the crystallographic analysis. In the case of TOF diffraction, the relation between patterns and the channel numbers can be adjusted by selecting the diffraction angle (2θ) to locate peaks at desired position to allow the analysis of specific peaks.

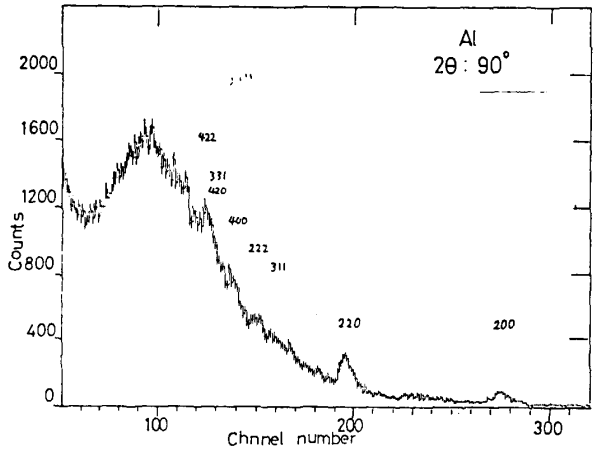

Fig. 5. Scattering of neutrons from polycrystalline aluminum.

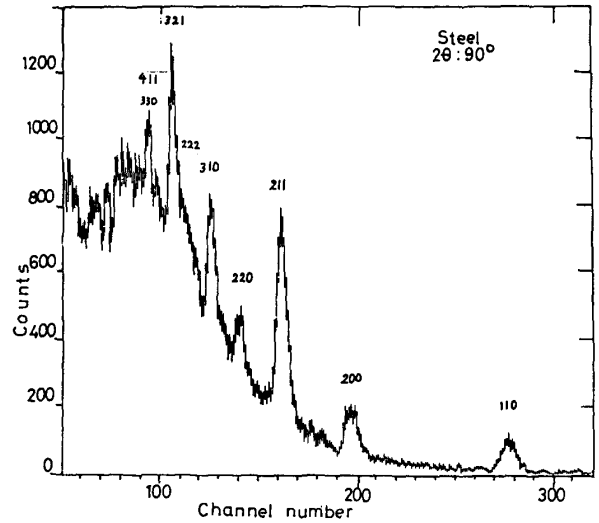

Fig. 6. Scattering of neutrons from polycrystalline iron.

IV. Measurements of transformation in RbBr under pressure.

As an example of measurements under pressure an observation is presented here on the transformation of RbBr from a NaCl-type structure to a CsCl-type. The specimen was RbBr, 98 % pure, powdered to pass 100 mesh, mixed with NaCl as a pressure indicator, of same purity, same size and one third in weight. Carbon disulfide (CS_2) was used as pressure transmitting medium, in every case no disturbance of CS_2 was observed in the pattern.

The diffraction patterns of RbBr only and of mixture of RbBr and NaCl are shown in Figs. 7 and 8. At lower pressures, the structure is NaCl-type and in the spectrum of mixed specimen peaks are separated and defined very well. At higher pressures, RbBr transforms into CsCl-type as shown in Fig. 9 and peaks for RbBr come near to those for NaCl.

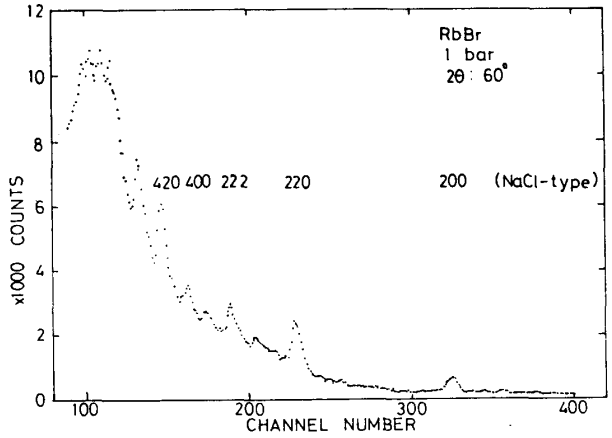

Fig. 7. Neutron diffraction of RbBr powder at 1 bar.

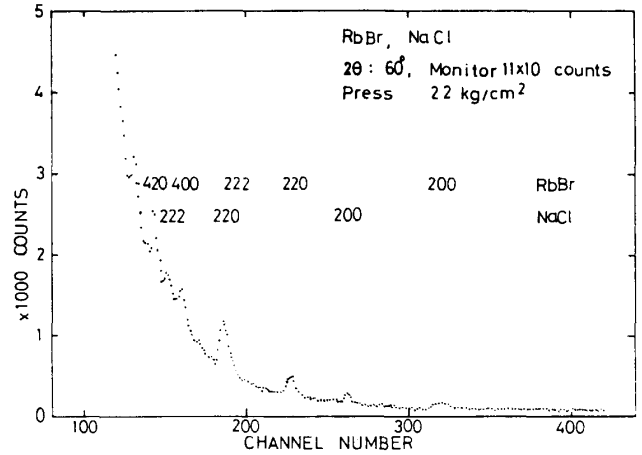

Fig. 8. Neutron diffraction of mixed powder of NaCl and RbBr, 1 : 3 in weight ratio, at low pressure.

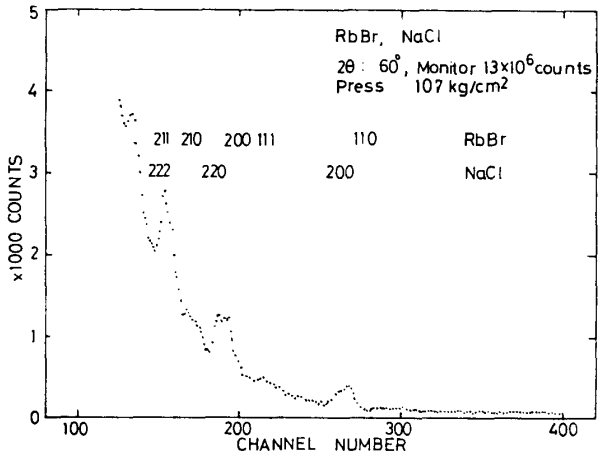

Fig. 9. Neutron diffraction in RbBr and NaCl mixture at high pressure, lines for RbBr are indexed as CsCl-type structure.

The pressure applied to the specimen is calculated from the change in lattice spacing of NaCl using Decker's results[6] and the volume change in RbBr is obtained from the pattern. Results of measurements are summarized in Table 1 and Fig. 10.

Table 1. The relation between pressures obtained by compression of NaCl and volume changes in RbBr.

Oil pressure kg/cm^2	NaCl $\Delta a/a_o$	Pressure kb	Crystal structure of RbBr	RbBr $\Delta V/V_o$
0	0	(1b)	NaCl	1.000
22	0.0059	4.3	NaCl	0.980
33	0.0070	5.3	NaCl	0.974
40	0.0078	5.5	CsCl	0.822
107	0.0135	10.7	CsCl	0.800
150	0.0170	13.8	CsCl	0.794
170	0.0197	16.3	CsCl	0.792

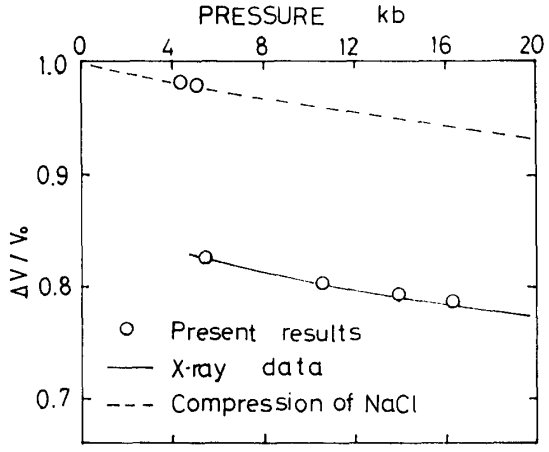

Fig. 10. Volume compression in RbBr.

The molar volume of RbBr is reduced with pressure at first, the rate being nearly the same with other alkalihalides, but an abrupt change of -15 % occurs at about 5.4 kb, at higher pressures the rate of contraction becomes small again. In Fig. 10, the present values are expressed by circles and the values obtained by Vaiya and Kennedy[7] using X-ray diffraction by a solid line. The correspondence of both data is good but some deviation is remarked at higher pressures. This will have a connection with the intervening of peaks of RbBr and NaCl at higher pressures and the accuracy of pressure determination is affected. The dashed line is the compression curve for NaCl and many alkalihalides have the similar value including RbBr as shown in Fig.10.

V. Discussion

The high pressure apparatus for the neutron diffraction in TOF methods was developed with satisfactory success. The Ti-Zr alloy is confirmed to be useful as a material for the pressure vessel. The incoherent scattering of neutron beams from the alloy expresses the energy distribution of the incident beam, and the value will be used to normalize the intensity of peaks diffracted from the specimen. The calculation can be made using one pattern obtained at one time for incident beam and scattered peaks.

But, of course, the high background and its statistical roughness perturb the diffraction patterns. Such disadvantage must be evaluatedin comparison with advantages mentioned above practically.

The selection of the pressure indicator is also important, the situation is same for the ordinary angular scanning method of diffraction in both neutrons and X-rays. In the present case of RbBr, KCl will be useful instead of NaCl. The relation of patterns in RbBr, NaCl and KCl are shown in Fig. 11.

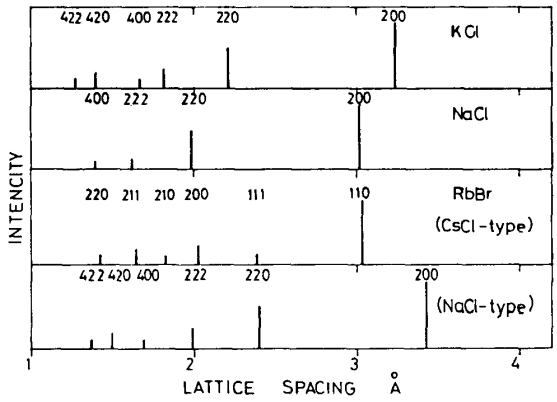

Fig. 11. The relation between lattice spacing and diffraction lines in RbBr, NaCl and KCl.

In connection with the transformation of RbBr induced by pressure, the mechanisms of transformation between NaCl-type and CsCl-type are discussed by many people. The detailed observation on single crystal is neccessary and the present method using Ti-Zr alloy cell will be effective for this purpose, because it gives no excess peaks. The combination of position-sensitive detector and the TOF method of neutron diffraction will be applied for the study of atomic movement in the course of the structural transformation. Two-dimensional information of the reciprocal lattice is obtained by computor proccessing in every moment and the in si-tu observation will enable us to detect the atomic movement and some precursors of the phenomena.

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