Hydrogen vibration excitations of ZrH_{1.8} and TiH_{1.84} up to 21 GPa by incoherent inelastic neutron scattering

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Hydrogen vibration excitations of fluorite-type ZrH_{1.8} and TiH_{1.84} were investigated at pressures up to 21 and 4 GPa, respectively, by incoherent inelastic neutron scattering experiments. The excitations of both the samples were well described by quantum harmonic oscillator (QHO) over the entire pressure region of this study. The first excitation energies increased with increasing pressure, as described by the equations $E_1(\text{meV}) = 141.4(2) + 1.02(2)P$ (GPa) and E_1 (meV) = 149.4(1) + 1.21(8)P (GPa) for ZrH_{1.8} and TiH_{1.84}, respectively. Coupling with pressure dependence of lattice parameters determined by diffraction experiments, the relations between metal-hydrogen distance (d_{M-H}) and E_1 of ZrH_{1.8} and TiH_{1.84} at high pressures are found to be well described by the equations $E_1(\text{meV}) = 1.62(9) \times 10^3 d_{M-H}^{-3.32(7)}$ (Å) and E_1 (meV) = $1.47(21) \times 10^3 d_{M-H}^{-3.5(2)}$ (Å), respectively. The slopes of these curves are very steep compared to the previously reported trend in various fluorite-type metal hydrides at ambient pressure, suggesting that pressure and chemical substitution affect the hydrogen vibration excitations differently. The hydrogen wave function spreading estimated from the E_1 value assuming the QHO model showed the preferential shrinkage of the wave function to the tetrahedral site. The preferential shrinkage of the hydrogen atom shrinks more intensively than the tetrahedral site. The preferential shrinkage of the hydrogen atom shrinks more intensively than the tetrahedral site. The preferential shrinkage of the hydrogen atom shrinks more intensively than the tetrahedral site. The preferential shrinkage of the hydrogen atom shrinks more intensively than the tetrahedral site. The preferential shrinkage of the hydrogen atom shrinks more intensively than the tetrahedral site. The preferential shrinkage of the hydrogen atom shrinks more intensively than the tetrahedral site. The preferential shrinkage of the hydrogen atoms and the resulting confinement of the h

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I. INTRODUCTION

Metal hydrides have attracted considerable attention in terms of basic science as well as industrial application. The interests are growing since the recent discovery of super-hydrides with $T_{\rm C}$ comparable to room temperature at high pressures [1–4]. The vibrational behavior of hydrogen is indispensable for understanding such high $T_{\rm C}$ and the discovery of superconductors with a higher $T_{\rm C}$. Incoherent inelastic neutron scattering (IINS) is a powerful tool for investigating the hydrogen vibration of metal hydrides because of its sensitivity to the hydrogen atom and the ability to investigate both energy and Q dependence simultaneously.

Hydrogen occupation sites in metal lattices depend on the electron positivity/negativity of hydrogen relative to metal atoms: electropositive hydrogen atoms tend to occupy octahedral sites with larger electron density, whereas electronegative atoms tend to occupy narrow tetrahedral sites with smaller electron density [5]. Among various metal hydrides with hydrogen atoms at tetrahedral sites, metal hydrides with fluorite structure have been intensively investigated because of the characteristic hydrogen excitation well described by quantum harmonic oscillators (QHOs). Previous studies have revealed that the first excitation energy E_1 increases with decreasing the metal-hydrogen distances $d_{\text{M-H}}$, as expressed by E_1 (meV) = $414 d_{\text{M-H}}^{-1.5}(\text{\AA})$ [6] or E_1 (meV) = $282 d_{\text{M-H}}^{-1}(\text{\AA})$ [7]. However, the correct function form is still debatable due to the lack of a physical model and/or the complexity arising from different chemical species among various hydrides. IINS experiments at high pressures would be useful in clarifying it because pressure can continuously change $d_{\text{M-H}}$ without being affected by different chemical species.

Another interesting issue of hydrogen vibration in metal hydrides is anharmonicity of the local potential field of a hydrogen atom. Hydrogen excitation in fluorite-type hydrides is well approximated by the QHO model (i.e., excitation energy $E_j = j\hbar\omega$, j = 1, 2, 3...), but a closer look at the excitation energies to higher levels shows a slight deviation from the overtone of the first excitation energy. For example, the anharmonicity β defined in $E_j = j\hbar\omega + \beta(j^2 + j)$ is negative and positive for hydrides with hydrogen atoms at tetrahedral and octahedral sites, respectively [8], implying that the local potential field is more or less deviated from the parabolic shape ($\beta = 0$). However, the dependence of the host metal lattice or the hydrogen site dimension is still unknown. Even if the state-of-the-art *ab initio* calculations are employed, it is difficult to reproduce the anharmonicity because of the

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quantum nature of hydrogen atoms [9,10]. The experimental investigation of anharmonicity at high pressures helps us understand them.

Despite the effectiveness of the IINS experiments, its practical application in high-pressure studies is rare because of weak sample signals due to the limited sample volume and strong attenuation by high-pressure cells. Thus far, two highpressure experiments have been reported [11,12], but the pressure range of the investigations was restricted only to 3 GPa, and further extension is required to observe significant pressure-induced changes. In this study, we have extended the pressure range to seven times higher by developing experimental techniques and applied them to fluorite-type $ZrH_{1.8}$ and $TiH_{1.84}$ showing almost ideal QHO behavior at ambient pressure; then we discuss pressure (or d_{M-H}) effects on the excitation energies and anharmonicity in these hydrides based on the results.

II. EXPERIMENT

A. Characterization of sample

The zirconium dihydride powder was purchased from Sigma-Aldrich Co. Ltd. The hydrogen composition was determined by both thermogravimetric (TG) analysis and neutron diffraction, independently. TG analysis was performed at temperatures up to 1273 K with the simultaneous thermal analyzer (NETZSCH STA449 F3 Jupiter), and the result revealed a hydrogen composition of x = 1.75. Neutron diffraction was performed at high-pressure neutron beamline PLANET in Materials and Life Science Experimental Facility (MLF), J-PARC [13]. The structure refinements revealed that the sample has a tetragonally distorted fluorite structure (space group, I4/mmm) with a hydrogen composition of x = 1.8(1). Both hydrogen compositions were consistent within the experimental uncertainty (hereafter, the chemical composition of zirconium hydride is referred to as ZrH_{1.8} for simplicity). These results indicate that the initial sample is the ε phase reported previously [14].

Titanium dihydride powder was purchased from Kojundo chemical laboratory Co. Ltd. The hydrogen composition was determined as 1.84 via TG analysis. Synchrotron x-ray diffraction experiments at BL22XU in SPring-8 revealed that the structure has a cubic lattice, indicating that the initial sample is the δ phase reported previously [15].

B. Confirmation of high-pressure states by diffraction

Prior to the IINS experiments, *in situ* high-pressure neutron and x-ray diffraction experiments were conducted on $\text{ZrH}_{1.8}$ and $\text{TiH}_{1.84}$, respectively, to confirm the phases observed in the IINS experiments at high pressures and determine the pressure dependence of lattice parameters.

Neutron diffraction experiments on $ZrH_{1.8}$ were conducted up to 23 GPa at PLANET. The sample was compressed with the Paris-Edinburgh (PE) press (MG63, VX4 [16]) equipped with double toroidal anvils made of sintered diamonds. Detailed experimental and data-reduction procedures are described in Ref. [17,18]. The results showed that the ε phase is stable over the entire pressure region of this study. The pressure dependence of the unit cell volume was well described by the second-order Birch-Murnaghan equation of state (EOS) with $K_0 = 118.6(8)$ GPa, and the axial ratio changed with pressure as expressed by c/a = 0.8939(3) - 0.00193(3) P(GPa) (see Figs. S1 and S2 in the Supplemental Material [18]). These results were in best agreement with those reported by Huang *et al.* [19], among several studies [19–21]. These pressure dependencies were used to estimate the metal-hydrogen distance d_{M-H} of ZrH_{1.8} at pressures at which the IINS data were collected.

In situ x-ray diffraction experiments on TiH_{1.84} were conducted up to 8.6 GPa at BL22XU at SPring-8. The powder sample was loaded in the gasket hole, along with a 4:1 methanol-ethanol mixture and a ruby pressure marker, and compressed using a diamond anvil cell with the culet diameters of 0.6 mm. The diffraction patterns revealed that the cubic δ phase transforms into the tetragonal ε phase by compression from 0.1 MPa to 0.9 GPa. The pressure dependence of the unit cell volume of the ε phase was well described by the secondorder Birch-Murnaghan EOS with $K_0 = 125.3(19)$ GPa, and the axial ratio changed with pressure by c/a = 0.928(2) + $0.054(1) \exp[-P(\text{GPa})/5.7(5)]$ (see Figs. S1 and S2 in the Supplemental Material [18]). The EOS and pressure dependence of the c/a ratio were almost identical to those obtained for TiH₂ by Kalita *et al.* [22], among several studies [22,23]. These pressure dependencies were used to estimate the metalhydrogen distance d_{M-H} of TiH_{1.84} at pressures at which the IINS data were collected. In addition to the x-ray diffraction, neutron diffraction was also conducted at high-intensity neutron total scattering beamline NOVA in MLF, J-PARC to determine the sample pressure and cross check the phase appearing in IINS experiments. The diffraction data were collected after each IINS measurement by retracting Fermi chopper from the incident beam path. The detailed methods of sample loading and compression are described in the next section. The neutron diffraction experiments confirmed that the IINS data of TiH_{1.84} above 0.9 GPa were collected in the ε phase.

C. Incoherent inelastic scattering measurements

IINS experiments of ZrH_{1.8} were conducted at the 4D-Space Access Neutron Spectrometer 4SEASONS in J-PARC [24]. In the measurement at ambient pressure, the powder sample was wrapped with an aluminum foil and attached to a top-loading stick. In the high-pressure measurements, the powder sample was loaded in the TiZr encapsulating gaskets along with the pressure transmitting medium of the 4:1 deuterated methanol-ethanol mixture, and then compressed with the PE press (MG63, VX5 [16]) equipped with single or double toroidal anvils. No chemical reaction of the sample with the pressure transmitting medium was confirmed beforehand in the neutron diffraction experiments (see Fig. S3 and Table S1 in the Supplemental Material [18]). The press was attached to our low-temperature and high-pressure (LTHP) system equipped with a 4 K Gifford-McMahon refrigerator, though all measurements were conducted at room temperature. The anvil surface and press pillars were shielded with a Cd foil to avoid unwanted scattering, followed by the insertion of the LTHP system in the vacuum chamber of 4SEASONS. The incident beam was truncated into a size of 14 mm in



FIG. 1. The setups of incoherent inelastic neutron scattering experiments at 4SEASONS (upper) and NOVA (lower).

width and 8 mm in height with a beam narrower, and the unwanted scattering was eliminated using radial collimators with a scattering gauge length of approximately 19 mm at 90° [25,26] (Fig. 1). IINS data were collected at pressures up to 21 GPa with incident neutron energies of $E_i = 660$, 266, 143, and 44 meV by employing the multi $-E_i$ method [27]. The background data were corrected in the separated runs by compressing only the pressure transmitting medium to identical pressure of the sample measurement. The typical exposure times for each measurement were 16 and 24 h for the experiments using single and double toroidal anvils, respectively. Raw data were transformed into S(Q, E) spectra using the UTSUSEMI software [28], and the background data were subtracted from the sample data. Energy spectra I(E) were obtained by integrating S(Q, E) along the Q direction. Raw data before and background subtraction are shown in Figs. S4 and S5 (Supplemental Material [18]). The pressure was estimated from the load applied to the anvils based on the predetermined calibration curve [17]. The pressure uncertainties were estimated from the uncertainty of the calibration curves and load applied to the anvils.

IINS experiments on $TiH_{1.84}$ were conducted at NOVA. In the ambient-pressure measurement, the powder sample was loaded in a vanadium can. In the high-pressure measurements, the sample was loaded in the same way as that for $ZrH_{1.8}$



FIG. 2. Representative S(Q, E) of $ZrH_{1.8}$ at high pressures taken with (a) $E_i = 266$ meV and (b) $E_i = 660$ meV. The Q, E resolution is degraded for easy recognition.

and compressed with a PE press (MG63, VX4), equipped with the single toroidal anvils. The body of the PE press was covered with a baked mixture of B₄C powder and epoxy resin to reduce the background. The press was attached to the flange developed for high-pressure experiments at NOVA [29] and inserted in the NOVA vacuum chamber. The incident beam was truncated into a size of 10 mm in width and 6 mm in height with a BN collimator, followed by the adjustment of the beam position to the sample using a motorized XZ stage. The incident beam and scattering neutron path were collimated with neutron shielding ducts made of a baked mixture of B₄C powder and epoxy resin to reduce the background (Fig. 1). The data were collected at ambient pressure, 0.9 and 4.0 GPa with the incident neutron energy of $E_i = 875$ and 216 meV. The background data were collected by the same way as that employed for the measurements of ZrH_{1.8}. The typical exposure time for the data collection at high pressures was 11–14 h. The obtained data were reduced into S(Q, E) spectra or I(E)similar to those for ZrH_{1.8}. Raw data before background subtraction are shown in Figs. S6 and S7 (Supplemental Material [18]). The pressure was calculated from the lattice parameter of TiH_{1.84} based on the EOS determined by the synchrotron x-ray diffraction experiments.

III. RESULTS

A. IINS of ZrH_{1.8}

Figure 2 shows S(Q, E) of ZrH_{1.8} taken at high pressures with $E_i = 266$ and 660 meV. Fig. 3 shows the energy spectra I(E) obtained by integrating S(Q, E) along the Q direction. The hydrogen vibration excitations characteristic of QHO are clearly observed. I(E) with $E_i = 266$ meV at ambient pressure shows a broad and asymmetric peak, composed of at least three components, indicated by arrows in the figure. This feature is consistent with previous experimental [9,10,31–33] and theoretical studies [10,34,35]. The calculated phonon dispersion indicates that the peak splitting is contributed by several phonon branches. With increasing



FIG. 3. I(E) of ZrH_{1.8} at high pressures with (a) $E_i = 266$ meV and (b) $E_i = 660$ meV. The energy resolutions at the bottom are calculated on the basis of Ref. [30].

pressure, the peak shifts toward high energies. To illustrate the shift more quantitatively, the profile is fitted with a single Gaussian peak as the energy resolution is insufficient to distinguish among the peaks. Fig. 4 shows the pressure dependence of the first excitation energy E_1 . E_1 monotonically increases with pressure, and the relation is expressed by the equation E_1 (meV) = 141.4(2) + 1.02(2) *P*(GPa). Using the unit cell volume at high pressures, the Grüneisen parameter of hydrogen vibration (mode gamma, $\frac{\partial \ln \omega_i}{\partial \ln V}$) is determined as $\gamma_i = 1.01(2)$ [see Fig. S8(a) in the Supplemental Material [18]]. The increase in E_1 by volume reduction is consistent with the trend in the ambient phases of zirconium hydrides with different hydrogen compositions [31] or that of γ -ZrH at high pressures [11].

B. IINS of TiH_{1.84}

Figure 5 illustrates the S(Q, E) of TiH_{1.84} taken with $E_i = 216$ and 875 meV. The energy spectra I(E) at each pressure are shown in Fig. 6. Similar to ZrH_{1.8}, the excitations characteristic of QHO are clearly observed in both the ambient δ phase and high-pressure ε phase. I(E) with $E_i = 216$ meV



FIG. 4. Pressure dependence of the first excitation energy in $ZrH_{1.8}$.



FIG. 5. Representative S(Q, E) of TiH_{1.84} at high pressures taken with (a) $E_i = 216$ meV and (b) $E_i = 875$ meV.

shows that the first excitation peak is composed of at least three components, denoted by E_{1a} , E_{1b} , and E_{1c} in both δ and ε phases. This feature is consistent with the previous studies on various titanium hydrides [11,32,36,37]. No significant change in the peak shape is observed by compression to 0.9 GPa despite the cubic-tetragonal transition. Both the splitting in the cubic δ phase and no profile change by δ - ε transition indicate that the splitting is not related to tetragonal distortion of the hydrogen site, but attributed to the dispersion of the optical branches [37].

With increasing pressure, the peaks shift toward higher energies. The observed pressure-induced hardening of hydrogen vibration is consistent with the previous high-pressure study on γ -TiH [11]. Peaks in I(E) at $E_i = 216$ meV are fitted with the sum of three Lorentzian functions to quantify the extent of the shift, wherein the Lorentzian function is used because the elastic peak at E = 0 meV is well described by the Lorentzian function. The center of gravity of the peak E_{1g} is also determined by fitting the entire profile with a single Gaussian



FIG. 6. I(E) of TiH_{1.84} at high pressures with (a) $E_i = 216 \text{ meV}$ and (b) $E_i = 875 \text{ meV}$. The energy resolutions at the bottom are calculated on the basis of Ref. [30].



FIG. 7. Pressure dependence of the first excitation energy in $\text{TiH}_{1.84}$.

function for the direct comparison with the results of $ZrH_{1.8}$. Fig. 7 shows the pressure dependence of the first excitation energy. The three peaks shift in almost the same manner and the pressure dependence of the center of gravity is described by E_{1g} (meV) = 149.4(1) + 1.21(8) *P*(GPa). Using the unit cell volume determined by diffraction, the Grüneisen parameter of hydrogen vibration (mode gamma) is determined as $\gamma_i = 1.11(8)$ [see Fig. S8(b) in the Supplemental Material [18]]. When compared with the results of ZrH_{1.8}, E_{1g} and the pressure-induced shift are larger than the corresponding values of ZrH_{1.8}.

IV. DISCUSSION

A. Perception of the hydrogen excitation

Before discussing the results of our IINS experiments, we briefly introduce how the hydrogen vibration excitations of metal hydrides have been understood thus far [6]. In metal hydrides with low hydrogen content, hydrogen rarely occupies the neighboring sites; hence, each hydrogen atom behaves as if individually vibrating in the local potential field formed by the metal lattice (i.e., local vibration at a single site). However, with the increasing hydrogen content, its probability of occupying the neighboring sites increases, and H-H interaction becomes non-negligible. Finally, when the hydrogen composition reaches 2, i.e., when all tetrahedral sites are occupied by hydrogen atoms, hydrogen atoms form a sublattice with respect to the host metal lattice. In this case, all atoms participate in the phonon branches (cooperative movements of all atoms). In practice, optical phonon branches are well separated from acoustic branches in energy as hydrogen atoms are significantly lighter than metal ions. Then, the optical phonon branches are approximated by the hydrogen sublattice vibration. This study on ZrH_{1.8} and TiH_{1.84} corresponds to the latter case. The first excitation peak of ZrH_{1.8} or TiH_{1.84} is explained by the optical phonon density of states obtained in theoretical studies [10,34,35,37].

Conversely, the higher energy excitations are understood by multiphonon excitations. The excitation energies are described by the overtones of the first excitation energy for a parabolic potential shape (i.e., only containing the secondpolynomial term), but not possible for nonparabolic potentials



FIG. 8. Relationship between $\Delta x(P)/\Delta x(0)$ and $d_{M-H}(P)/d_{M-H}(0)$. The relation expected for uniform contraction is shown by a dotted line.

including higher polynomial terms. When excited by high energy comparable to the depth of the hydrogen local potential, hydrogen is not confined in a single site and diffuses to a neighboring site. In an extreme case wherein hydrogen atoms are excited by a much larger energy, they cannot sense the local potential field and behave like free gas [8], and S(Q, E) shows a continuum expressed by $E = \hbar^2 Q^2/2M$, where *M* represents the proton mass [38].

B. Compressibility of hydrogen wave function

First, we evaluated the spreading of the hydrogen (proton) wave function to compare the dimension of the local potential field with that of the tetrahedral site. The excitation energy to the first energy level is low enough to be approximated by the harmonic oscillator. In the QHO model, the spreading of the wave function (Δx) is related to E_1 by the following equations [8,38]:

$$(\Delta x)^2 = \frac{\hbar}{2M\omega_0} = \frac{\hbar^2}{2ME_1}.$$
 (1)

 Δx at high pressures were obtained from E_1 using Eq. (1). The validity of the values obtained by this method was confirmed by the agreement of Δx of ZrH_{1.8} at 0.1 GPa [0.1207(1) Å] with the root of the mean square displacement of the excited hydrogen atoms reported in Ref. [10] (0.12 Å). The analysis revealed that Δx monotonically decreases with increasing pressure. To compare the compressibility between the proton wave function and the tetrahedral site, the ratios of hydrogen wave function spreading and metal-hydrogen distances relative to the respective values at ambient pressure are plotted in Fig. 8. The figure shows that the proton wave function is more compressible than the tetrahedral site in both hydrides. In other words, the potential field for a hydrogen atom shrinks more intensively than the interstices formed by the metal lattice. This can be understood by the following mechanism: the lattice contracts by the shrinkage of both the metal atom and the interstices, but the metal atom is less compressible; thus, the local potential field of the proton (or hydrogen atom) shrinks more intensively.



FIG. 9. Comparison of unit cell volumes of pure Zr [39] and $ZrH_{1.8}$ (this study) and the hydrogen induced volume calculated from them.

It is noteworthy that hydrogen induced volume shows a significantly different compressibility. Fig. 9 illustrates the pressure dependence of unit cell volume per Zr atom of pure Zr and ZrH_{1.8} and hydrogen induced volume $\Delta V_{\rm H} (= V_{\rm ZrH1.8} - V_{\rm Zr})$ calculated from them. Here, the unit cell volume of pure Zr (α - and ω -Zr) are based on Ref. [39], and that of ZrH_{1.8} is based on this study. The hydrogen induced volume per hydrogen $v_{\rm H} (= \Delta V_{\rm H} / 1.8)$ at ambient pressure is 2.45 Å³, which is consistent with previously reported value [2.6-3.1 Å³ (Ref. [8])]. With increasing pressure, $\Delta V_{\rm H}$ remains or slightly increases in spite of compression. This, however, does not necessarily mean that hydrogen is highly incompressible. It is due to the difference in chemical bonding between pure Zr and ZrH_{1.84}. Namely, when the transition metals are hydrogenated, covalentlike chemical bonding is formed by H 1s and Zr 4d orbitals [40]. The bulk compressibility of $ZrH_{1.8}$ is mainly controlled by the covalent bonds that are less compressible than conduction electrons (and d electrons) in pure Zr. This example alerts us that hydrogen induced volume calculated from the volume difference between pure Zr and zirconium hydrides is irrelevant to the hydrogen volume in the hydride.

C. Relation between d_{M-H} and E_1

As mentioned in the Introduction, excitation energies E_1 of the fluorite-type metal hydrides are strongly correlated with $d_{\text{M-H}}$. Fig. 10 shows the $d_{\text{M-H}}$ dependence of E_1 previously reported in various hydrides at ambient pressure [6,7]. Ross *et al.* [6]. reported a relation of E_1 (meV) = $414 d_{\text{M-H}}^{-1.5}(\text{Å})$ by fitting these data using the equation with the power of -1.5. Alternatively, Fukai and Sugimoto [7] reported a relation of E_1 (meV) = $282 d_{\text{M-H}}^{-1.6}(\text{Å})$ by assuming the power of -1 in the equation. Compared to these, the data of ZrH_{1.8} and TiH_{1.84} at high pressures showed a different behavior: E_1 values steeply increased at small $d_{\text{M-H}}$ and the relations for ZrH_{1.8} and TiH_{1.84} were determined as E_1 (meV) = $1.62(9) \times 10^3 d_{\text{M-H}}^{-3.32(7)}(\text{Å})$ and E_1 (meV) = $1.47(21) \times 10^3 d_{\text{M-H}}^{-3.5(2)}(\text{Å})$, respectively, by fitting the data with the equations without assuming the specific powers. The powers in these equations are similar to each other but



FIG. 10. Relationship between the average metal-hydrogen distance and the first excitation energy in various hydrides at ambient pressure [6,7] and $ZrH_{1.8}$ and $TiH_{1.84}$ at high pressures (this study).

significantly smaller than those reported by Refs. [6] and [7], suggesting that compression exerts a different effect on the hydrogen vibration excitations from that by the chemical substitution of the host metal lattice.

The theoretical $d_{\text{M-H}}-E_1$ relation [7] helps us to understand the origin of the difference. When a metal-hydrogen interatomic potential is expressed by the sum of the central pair potentials with the form of $u(r) = A \exp(-\alpha r)$ and a harmonic approximation is employed, the $d_{\text{M-H}}-E_1$ relation can be analytically expressed by

$$E_{1} = \hbar \alpha \sqrt{\frac{4A}{3M}} e^{-\frac{\alpha d_{\rm M-H}}{2}} \sqrt{1 - \frac{2}{\alpha d_{\rm M-H}}},$$
 (2)

where α is the decay parameter of metal-hydrogen interaction [7]. The data of $ZrH_{1.8}$ and $TiH_{1.84}$ at high pressures are well fitted with this equation, and the pair potentials of u(r) (eV) = $5.5(5) \times 10^2 \exp[-3.45(7) r(\text{\AA})]$ and $u(r) (\text{eV}) = 6.1(17) \times$ $10^2 \exp[-3.8(2) r(\text{\AA})]$ are obtained for ZrH_{1.8} and TiH_{1.84}, respectively (see Fig. S9 in the Supplemental Material [18]). The potential shape at the tetrahedral site in ZrH_{1.8} calculated using the pair potential qualitatively agrees with results of abinitio calculation [41] (see Fig. S10 in the Supplemental Material [18]). Therefore, the steep rise of E_1 at a small $d_{\rm M-H}$ likely comes from the invariance of potential parameters during the compression over the entire pressure region of this study. In contrast, the inverse relation of E_1 with respect to $d_{\rm M-H}$ in various metals hydrides was interpreted by increasing the decay parameter at a small d_{M-H} : Fukai and Sugimoto [7] explained that E_1 inversely changes with $d_{\text{M-H}}$ when α is proportional to $1/d_{M-H}$ as is obvious from Eq. (2). From these considerations, the different $d_{M-H}-E_1$ relations between pressure variation and chemical substitution are likely caused by the different behavior of the pair potential when d_{M-H} is decreased. In other words, pressure shrinks the local potential field of hydrogen atoms directly through the rigid metal ion core, whereas the chemical substitution moderately shrinks the local potential field accompanied by the decrease in the metal-hydrogen interaction range $(1/\alpha)$.



FIG. 11. Higher excitation energies of $ZrH_{1.8}$ at pressures below 6 GPa. The extended line of the first excitation energy at each pressure is also shown.

D. Anharmonicity of the local potential field

The excitations to higher energy levels are no more approximated by the harmonic oscillator. The anharmonicity of the potential field is reflected in the higher energy excitations. Fig. 11 shows j dependence of E_i of $ZrH_{1.8}$ determined by fitting peaks in I(E) with Lorentzian functions. The extended line of the first excitation energy at each pressure is also shown to easily observe the deviation. Here, only the data below 6 GPa are shown because those above 6 GPa that are taken with double toroidal anvils are less accurate due to the small sample size and resulting insufficient counting statistics of I(E) profiles. The higher excitation energies are found to be deviated from the extended line at any pressure, suggesting that the potential field around hydrogen atoms are anharmonic. All the E_i with $j \ge 2$ are located below the extended line, indicating that the potential shape is trumpetlike. This result is consistent with the result of $ZrH_{1.41}$ at ambient pressure [32].

In this study, anharmonicity is evaluated by using energies up to the third excitation. When hydrogen is located at a tetrahedral site in an fcc metal lattice, the local potential field expanded to fourth order is described by

$$U(X, Y, Z) = c_2(X^2 + Y^2 + Z^2) + c_4(X^4 + Y^4 + Z^4) + c_{22}(X^2 Y^2 + Y^2 Z^2 + Z^2 X^2),$$
(3)

where X, Y, and Z are the Cartesian coordinates, and c_2 , c_4 , and c_{22} are the force constants. Based on the first-order perturbation theory, the energy eigenvalues e_{lmn} are calculated as

$$e_{lmn} = \sum_{l,m,n} \{ \hbar \omega (j+1/2) + \beta (j^2 + j + 1/2) + \gamma [(2l+1)(2m+1) + (2m+1)(2n+1) + (2n+1)(2l+1)] \}.$$
(4)

Here, *l*, *m*, and *n* represent the quantum numbers of the vibration along *X*, *Y*, and *Z* directions, respectively, and *j* is the sum of them. ω , β , and γ are $\sqrt{2c_2/M}$, $3\hbar^2 c_4/4Mc_2$, and $\hbar^2 c_{22}/8Mc_2$, respectively (see Ref. [5]). The excitation energy to each *lmn* level is calculated by $E_{lmn} = e_{lmn} - e_{000}$,



FIG. 12. Pressure dependence of c_2 , c_4 , and c_{22} obtained from excitation energies in ZrH_{1.8} at pressures below 6 GPa.

written as

$$E_{100} = e_{100} - e_{000} = \hbar\omega + 2\beta + 4\gamma,$$

$$E_{200} = e_{200} - e_{000} = 2\hbar\omega + 6\beta + 8\gamma,$$

$$E_{110} = e_{110} - e_{000} = 2\hbar\omega + 4\beta + 12\gamma,$$

$$E_{300} = e_{300} - e_{000} = 3\hbar\omega + 12\beta + 12\gamma,$$

$$E_{210} = e_{210} - e_{000} = 3\hbar\omega + 8\beta + 20\gamma,$$

$$E_{110} = e_{110} - e_{000} = 3\hbar\omega + 6\beta + 24\gamma.$$
 (5)

Considering the degeneracy in energy levels, the average *j*th excitation energy E_i is represented by

$$E_{1} = \hbar\omega + 2\beta + 4\gamma, E_{2} = 2\hbar\omega + 14/3\beta + 32/3\gamma, E_{3} = 3\hbar\omega + 156/19\beta + 372/19\gamma.$$
(6)

Thus $\hbar\omega$, β , and γ are calculated from the observed excitation energies E_1 , E_2 , and E_3 based on the above three equations. Then, the force constants of c_2 , c_4 and c_{22} are derived from the obtained parameters.

Figure 12 demonstrates the pressure dependence of force constants of $ZrH_{1.8}$ at pressures up to 6 GPa. Near ambient pressure, c_4 and c_{22} values are close to zero, suggesting that the potential field is nearly harmonic. With increasing pressure, c_4 and c_{22} deviate from zero, indicating that anharmonicity increases with pressure. The pressure evolution of the potential shape calculated from the values at 0.1 MPa, 2.5 GPa, and 5 GPa that are shown in Fig. 13. Here, the force constants at respective pressures are calculated from



FIG. 13. Isopotential surface around hydrogen in $ZrH_{1.8}$ at 0, 2.5, and 5 GPa. Edge length of each cube is 0.8 Å. Contour at 100, 200, 300, 400 meV are shown.

the regression lines in Fig. 12. It is found that the isopotential surfaces are elongated along the 111 direction and the elongation increases with pressure. The trumpetlike potential shape is considered to originate from this elongation.

V. SUMMARY

We investigated the hydrogen vibration excitations of $ZrH_{1.8}$ and $TiH_{1.84}$ with fluorite structures at pressures up to 21 and 4 GPa, respectively, by IINS. The former is seven times higher than previous studies of metal hydrides [11,12]. The hydrogen vibration excitations were well described by the QHO model over the entire pressure region of the study. The first excitation energy increased with pressure, as described by the equations E_1 (meV) = 141.4(2) + 1.02(2) *P*(GPa) and E_{1g} (meV) = 149.4(1) + 1.21(8) *P*(GPa) for ZrH_{1.8} and TiH_{1.84}, respectively. The hydrogen wave function obtained from E_1 assuming QHO showed that the local potential field for hydrogen shrinks more intensively than the tetrahedral site

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of the host metal lattice. E_1 increased with a decrease in the average metal-hydrogen distance (d_{M-H}) at a larger rate than the $d_{M-H}-E_1$ relations in various metal hydrides with fluorite structures at ambient pressure. These would be attributed to the rigid metal ion core compared to hydrogen atoms and the resulting confinement of the hydrogen atom in the narrower potential field at high pressures. This study will stimulate further studies under pressure, advancing our understanding of the fundamentals of hydrogen vibration in metal hydrides.

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