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Neutron spectroscopy of $\text{TiH}_{0.74}$ after high pressure treatment

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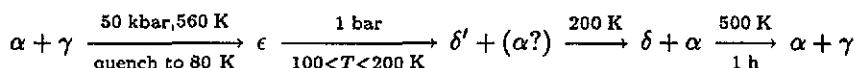
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Abstract. High resolution neutron scattering studies of vibrational spectra (2–800 meV) were carried out on the ϵ -, δ' - and δ -phases of titanium hydride, obtained after high pressure treatment. The observed splitting of the fundamental optic peak in the δ -phase spectrum can be explained by a strong H–H interaction along the c -axis. Well pronounced features are seen on the low energy side of the two- and three-phonon optic bands. These are assigned to bound bi- and tri-phonon excitations. This is the first observation of bi- and tri-phonons in metal hydrides.

1. Introduction

The T - x phase diagrams of the group IV metal–hydrogen systems are of a simple eutectoid type [1, 2]. Therefore, study of their crystal structures and vibrational properties was thought to be complete (e.g. see reviews [2, 3]). However, new phase equilibria have been observed in recent high pressure experiments on the Ti–H system [4–8].

Figure 1 represents the T - x diagram of the titanium–hydrogen system [1]. Here α is a solid solution of hydrogen in HCP titanium, β is a solid solution based on the high temperature BCC modification of titanium, and γ is a deficient dihydride with the FCC metal sublattice. Thermobaric treatment and subsequent quenching under high pressure resulted in a transformation of two-phase TiH_x samples ($0.70 \leq x \leq 0.75$) into the single-phase orthorhombic ϵ -phase [6, 7]. The sequence of further structural transitions [9–12] can be summarized by the following scheme:



where the conditions for the transformations are shown alongside the arrows.

The δ -phase is a nearly stoichiometric hydride TiH which has a face-centred orthorhombic lattice with only 1% difference in the lattice parameters a and b , but with

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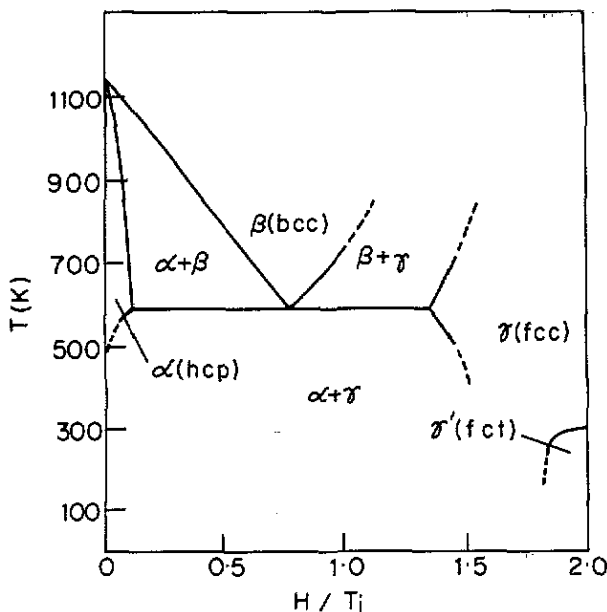


Figure 1. The Ti-H phase diagram [1].

$c/a \approx 1.09$ [11-13]. The ϵ -, δ' - and δ -phases have poor stability and transform at 1 bar irreversibly. Neutron scattering experiments [12, 14-16] have shown that hydrogen atoms in the ϵ -phase mainly occupy the octahedral positions of the metal sublattice. In the δ -phase hydrogen was only found in the ordered tetrahedral sites on alternate $\{110\}$ planes.

Recently the ϵ to $\delta + \alpha$ transformation in $\text{TiD}_{0.74}$ was studied by the simultaneous measurements of the (real time) neutron diffraction and small angle neutron scattering [12]. It was shown that an intermediate δ' -phase is formed from the ϵ -phase. The deuterium atoms are displaced from octahedral sites to ordered tetrahedral sites. The initial site occupancy in the δ' -phase was $P_D = 0.74$. The P_D value increased continuously on further heating, and 'pure' titanium precipitated. An enormous coefficient of thermal expansion along the c -axis ($\Delta c/(c\Delta T) \approx 10^{-4} \text{ K}^{-1}$) was explained by a strong D-D interaction in this direction.

The study of vibrational properties was further stimulated by an enhanced superconductivity, and an inverse isotope effect on superconducting temperatures, T_c , in the ϵ -phase. These T_c values gradually decrease in the δ' -phase, and there is a complete lack of superconductivity in δ - TiH_x [7, 9, 15]. The inverse isotope effect on T_c has been observed for some other hydrides [3]. It was explained in terms of the anharmonicity of the H(D) vibrations [17] or by excitations within a two-level system [18-20].

Previous inelastic neutron scattering (INS) experiments [14-16] were carried out with modest spectral resolution $\Delta\omega/\omega \approx 10\%$. The reported spectrum of the ϵ -phase of titanium hydride consisted of a very broad optical band at the rather low frequency of $\omega_o = 71$ to 75 meV (full width at half maximum, $\Delta_o = 37$ to 44 meV). This should be compared with the spectrum of the δ -phase ($\omega_T = 155$ to 157 meV, $\Delta_T = 27$ to 30 meV). The increased band width, Δ_o , can be indicative of (i) a strong dispersion of the hydrogen vibrations in the octahedral sites; (ii) a wide distribution of local

hydrogen potentials at the octahedral positions (due to the deficiency of the hydride); or (iii) lattice distortion in the ϵ -phase.

In this paper we describe our more detailed investigation of the INS spectra of the new phases of titanium hydride. These spectra cover a wide region of neutron energy transfer with high resolution. Some unusual features in the spectrum of the δ -phase are reported.

2. Experimental details

The sample was synthesized by saturating a high purity titanium with hydrogen gas (obtained from the thermal decomposition of TiH_2). The hydrogen content was determined from increases in the weight and gave $\text{TiH}_{0.74 \pm 0.01}$.

The ϵ -phase was produced at the Institute of Solid State Physics Academy of Science, USSR by compressing the sample to 60 kbar and heating to 620 K. It was rapidly quenched (20 s) to about liquid nitrogen temperatures and the pressure was then lowered to atmospheric [6-8]. All intermediate procedures and storage involving the ϵ -phase sample were carried out under liquid nitrogen. The δ' - and δ -phases were obtained by heating the ϵ -phase to 148 and 290 K, respectively.

The INS spectra were obtained at 35 K using the time-focused crystal analyser spectrometer TFXA [21] at the spallation neutron source, ISIS, Rutherford Appleton Laboratory, UK. This is an inverted geometry spectrometer with fixed analyser neutron energy of approximately 4 meV. The spectrometer provides good energy resolution ($\Delta\omega/\omega \leq 2.0\%$ over the energy transfers of interest: 2 to 500 meV). The neutron scattering angle was approximately 135° . An empty cryostat background was subtracted from the data, which were transformed by standard programs to $S(Q, \omega)$ against energy transfer (meV).

3. INS spectra

The experimental spectra of the ϵ -, δ' - and δ -phases of $\text{TiH}_{0.74}$ at 35 K are shown in figure 2. The parameters of the observed fundamental optical peaks are listed in table 1. Comparison with the previous data [14, 15] reveals good agreement between the reported positions of the fundamentals.

Table 1. Positions, widths and intensities of the fundamental bands observed in the INS spectrum of the ϵ -, δ' - and δ -phases of $\text{TiH}_{0.74}$.

	ω_0 (meV)	Δ_0 (meV)	I_0^b	$\omega_T(1)$ (meV)	$\Delta_T(1)$ (meV)	$I_T(1)^b$	$\omega_T(2)$ (meV)	$\Delta_T(2)$ (meV)	$I_T(2)^b$	$I_T(1) + I_T(2)^b$
ϵ	78.0	30.3	3.1	153.3	9.7	6.6	168.5	6.1	1.6	8.2
δ'	72.4	31.2	1.4	152.7	7.5	7.8	167.1	7.7	3.3	11.1
δ	—	—	—	153.5	4.8	8.6	167.6	5.9	2.8	11.4
δ -MLPH ^a	—	—	—	154.1	5.4	—	167.7	6.1	—	—

^a Parameters for the δ -phase refer to the multi-phonon corrected spectrum (see text).

^b Arbitrary units.

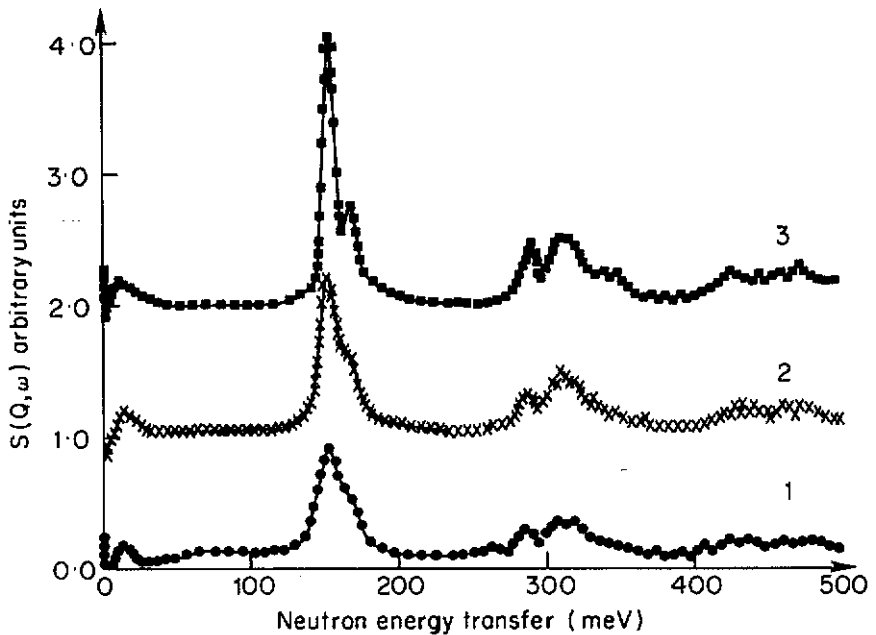


Figure 2. The INS spectra for (1) $\epsilon + (\delta')$, (2) δ' and (3) δ -phases of titanium hydride $\text{TiH}_{0.74}$ as measured on TFXA at 35 K.

The ϵ -phase exhibits a broad optical band at $\omega_o = 78$ meV, with $\Delta_o = 30.3$ meV. This band is related to vibrations of hydrogen atoms distributed on the octahedral interstitial sites. The sharp feature at 160 meV associated with hydrogen vibrations in tetrahedral sites, however, is indicative of a partial ϵ to δ' transformation in this sample. This probably occurred because the temperature of this measurement was close to the limit for thermal stability of the ϵ -phase. Therefore, we shall draw no conclusions about the anharmonicity of the ϵ -phase from this spectrum.

A clearly observed internal structure is present for all phonon bands in the δ -phase (curve 3 in figure 2). The fundamental, ω_T , is split into two lines $\omega_T(1)$ and $\omega_T(2)$. These have an intensity ratio of about 3:1. A similar structure is also characteristic of the δ' -phase spectrum. These ω_T peaks are less resolved than those of the δ -phase. The INS intensity at about 75 meV indicates that hydrogen atoms partially occupy octahedral sites. It can be seen from the data that the intensity of the ω_o peak decreases continuously, to zero, during the $\epsilon \rightarrow \delta' \rightarrow \delta$ transformations. This is due to the displacement of hydrogen atoms from octahedral to tetrahedral positions. There is a corresponding increase in the intensity of the ω_T peak. The width of the $\omega_T(1)$ peak is halved during the evolution of the δ' -phase, but no qualitative changes were observed. This decrease in the width of $\omega_T(1)$ probably arises from the increase of order as the non-stoichiometric δ' - $\text{TiH}_{0.74}$ evolves and transforms to stoichiometric δ -TiH.

3.1. INS spectrum of δ -phase: one-phonon features

The experimental δ -phase spectrum exhibits several bands at high energy transfers. The frequencies of these bands are roughly integer multiples of ω_T . The areas under the fundamental and the following band, $\omega \simeq 300$ meV, are in the ratio 1:0.76. This is in good agreement with the ratio 1:0.74 which was derived for the intensities of

the harmonic hydrogen oscillator [22]. the $\omega_{\text{T}}(1)$ and $\omega_{\text{T}}(2)$ have positions that are close to those for hydrogen vibrations on tetrahedral sites in other phases of group IV metals. We may conclude therefore that the fundamental optical band of these hydrogen vibrations falls in the range 140 to 180 meV. The other bands (270 to 370 meV and 400 to about 500 meV) can then be attributed to two- and three-phonon neutron scattering processes. The intensity ratio of the $\omega_{\text{T}}(1)$ and $\omega_{\text{T}}(2)$ bands can be estimated from site symmetry considerations. The simplest model involves hydrogen to nearest-metal central forces. For a distorted tetrahedral site (with a metal lattice parameter ratio of $c/a = 1.09$), such a model predicts the ratio of the intensities to be $I_{\text{T}}(1)/I_{\text{T}}(2) = \frac{1}{2}$, with a frequency ratio of $\omega_{\text{T}}(2)/\omega_{\text{T}}(1) = \sqrt{c/a} = 1.044$.

As we observed $I_{\text{T}}(1)/I_{\text{T}}(2) = 3$ and $\omega_{\text{T}}(2)/\omega_{\text{T}}(1) = 1.088$ (cf the c/a ratio), this model can be dismissed. An alternative model, involving the next nearest neighbours (the hydrogen atoms) may be more appropriate. The hydrogen sublattice has a tetragonal structure with lattice parameters \bar{c} and \bar{a}

$$\bar{c}/\bar{a} = (c/2)/(a\sqrt{2}/2) = 0.77.$$

This should lead to a strong H-H interaction along the c -axis [12] producing significant dispersion of the $\omega_{\text{T}}(2)$ mode. One possible dispersion of the ω_{T} branches is schematically represented in figure 3. We believe that the observed intensity distribution of the δ -phase should be explained in this manner, and $\omega_{\text{T}}(2)$ arises from oscillations along the c -axis.

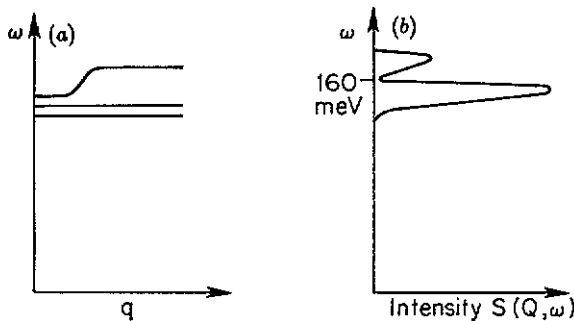


Figure 3. Schematic representation of (a) the dispersion of optical modes ω_{T} and (b) their intensity $S(Q, \omega)$ for the δ -phase of TiH . This is used to describe the observed intensity ratio (see text).

The generalized vibrational density of states $G(\omega)$ is given by

$$G(\omega) = \frac{1}{Q^2} \frac{\omega}{(n(\omega) + 1)} \exp(2W) S(Q, \omega) \quad (1)$$

where Q is the neutron momentum transfer; $n(\omega)$ the Bose occupation factor; and $2W$ the Debye-Waller factor. In the region of the lattice vibrations $G(\omega)$ is shown in figure 4. Characteristic peaks at about 13.5 and 21 meV appear to be associated with the transverse acoustic modes near the edge of the Brillouin zone. The spectrum cuts off at about 45 meV. The low frequency part of the spectrum from 2 to 11 meV can be understood within the Debye model, $G(\omega) = \alpha\omega^2$. The Debye temperature, $\Theta_{\text{D}} = 29.2$ meV, is determined by equating the area under the calculated $\alpha\omega^2$ curve to that under the experimental $G(\omega)$ curve up to 45 meV. For comparison, the Debye temperature of $(\alpha + \gamma)\text{-TiH}_x$ ($0 < x \leq 1.6$) ranges from 36.7 to 33 meV, but this rapidly decreases to 20.5 meV for $\gamma\text{-TiH}_{2-x}$ (see [2]).

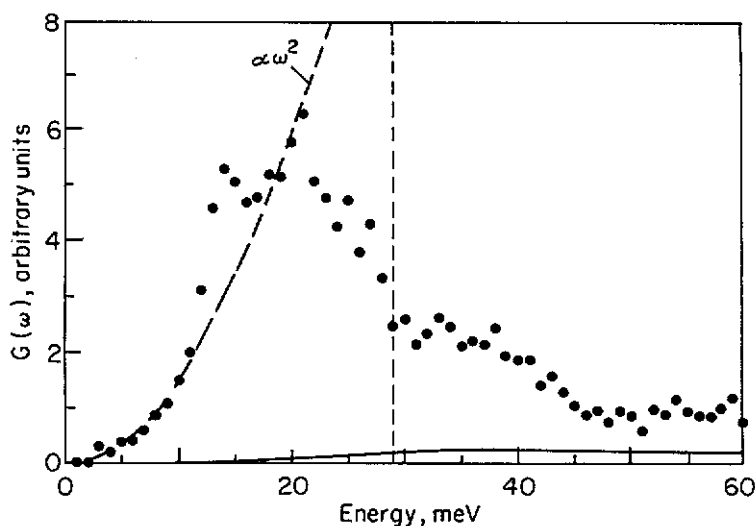


Figure 4. The generalized vibrational density of states $G(\omega)$ of δ -TiH in the energy region of lattice vibrations: points, experimental data; full line, calculated multi-phonon neutron scattering contribution; and broken line, Debye model $G(\omega) = \alpha\omega^2$.

3.2. Multi-phonon neutron scattering for the δ -phase spectrum

All INS spectra of the titanium hydride phases show strong multi-phonon contributions and can be described in terms of scattering from the hydrogen atoms alone. It has been shown [23, 24] that the intensities of the multi-phonon processes can be calculated within the harmonic approximation, by the appropriate convolution of the generalized vibrational density of states.

This technique has been applied to the INS spectra of organic crystals [23, 24] using a calculated one-phonon $G(\omega)$.

We have used this method to obtain the one-phonon $G(\omega)$. This was extracted from the experimental spectrum of δ -TiH by an iterative procedure. In the initial step, the experimental $G(\omega)$ was normalized to unity in the frequency region from 140 to 180 meV. (Note however that the whole spectrum from 2 to 200 meV was taken as the one-phonon spectrum.) The calculated multi-phonon contribution was subtracted from the spectrum which was then normalized again in the region of ω_T . The procedure was iterated until the one-phonon and calculated multi-phonon spectra showed no further change. This method has been successfully applied recently to describe the INS spectra of $\text{MnH}_{0.86}$, $\text{NiH}_{1.05}$ and $\text{PdH}_{0.99}$ [25, 26].

Only three iteration cycles were necessary to reach the required convergence. The results (figures 5 and 6) indicate that the high frequency shoulder of the ω_T peak can be completely explained by two-phonon (acoustic plus optic) neutron scattering, or 'phonon wing'. The contribution of two-phonon (acoustic plus acoustic) neutron scattering processes to the spectrum in the region of lattice vibrations is negligible, as shown in figure 4. The positions and widths of the $\omega_T(1)$ and $\omega_T(2)$ peaks remain almost unchanged by these multi-phonon corrections.

In the high energy regions, the calculated two- and three-phonon bands did not fit all of the spectral details (see figure 6). An unexpected sharp peak, at $E_2 = 286.6$ meV (width $\Delta E_2 = 5.4$ meV) and a broad band at $E_3 = 428.8$ meV (width $\Delta E_3 = 19.3$ meV) were observed. These band positions were to considerably lower

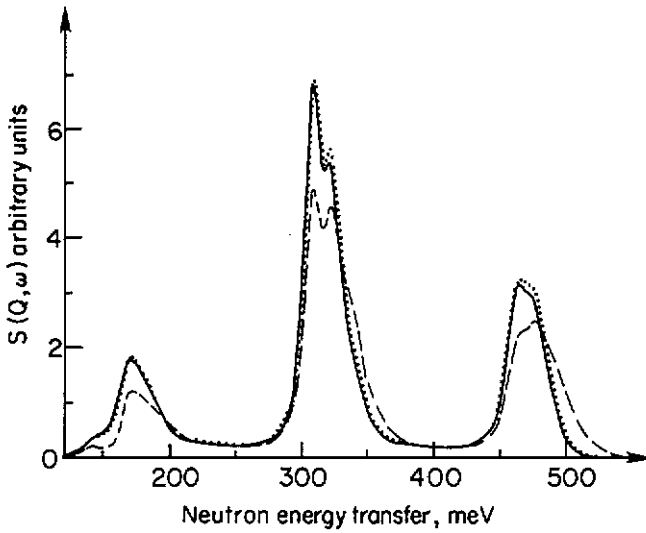


Figure 5. Calculated multi-phonon neutron scattering spectra of δ -TiH for different iterations.

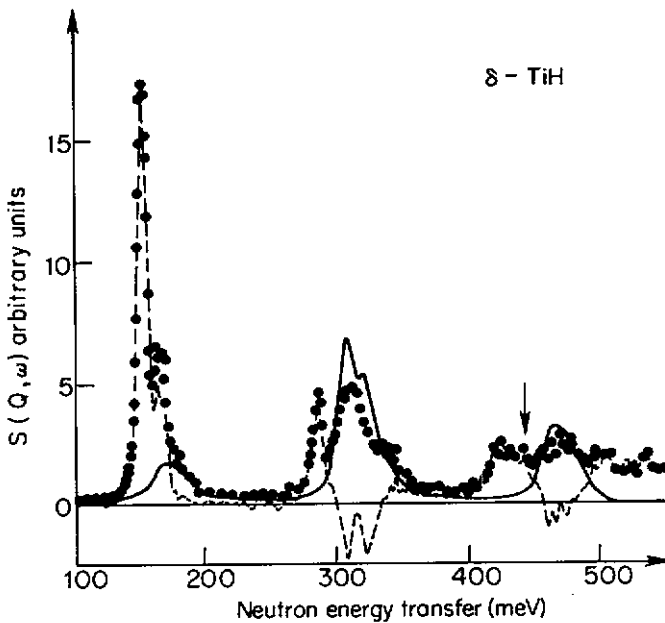


Figure 6. The $S(Q, \omega)$ spectrum for δ -TiH at 35 K showing the measured spectrum as points, the calculated multi-phonon neutron scattering contribution as a full line and the difference between the experimental spectrum and multi-phonon calculation as a broken line.

energy than any harmonic estimates, i.e. the system is strongly anharmonic. This anharmonicity can be simply parameterized by

$$\sigma_n = E_n - n\omega_T. \quad (2)$$

Therefore $\sigma_2 = -21.6$ meV and $\sigma_3 = -33.5$ meV for $\omega_T = \omega_T(1)$, and $\sigma_2 = -48.8$ meV and $\sigma_3 = -74.3$ meV for $\omega_T = \omega_T(2)$.

4. Bound multi-phonon excitations

The nature of the observed anharmonicity can be modelled by a strong interaction between optic phonons. This interaction results in the formation of bound multi-phonon states, called bi- and tri-phonons. In this model there is no requirement for the formation of any new states in the region of the fundamental. These bound multi-phonon excitations appear in the spectrum as separate features. They are located close to the continua of the unbound two- and three-phonon states, but to lower energies. Excitations of this type have been observed previously in the light scattering spectra of several molecular crystals. An extensive theoretical background for these bound states has been developed [27–32].

Our model consists of a Hamiltonian of the form [28]

$$\hat{H} = \sum_n \omega B_n^+ B_n + \sum_{n \neq m} V_{nm} B_n^+ B_m - A \sum_n (B_n^+)^2 (B_n)^2 - \tilde{A} \sum_n (B_n^+)^3 (B_n)^3 \quad (3)$$

where ω is the frequency of the anharmonically renormalized hydrogen vibration. B_n^+ (B_n) are the Bose creation (annihilation) operators for a vibrational quantum on the n th hydrogen atom. V_{nm} is a matrix element of the energy operator for the interaction of hydrogen atoms n and m , it corresponds to the transfer of one quantum of vibration from atom n to atom m . The anharmonicity constants A and \tilde{A} determine the strengths of the two- and three-particle interactions. The energies of the bi- and tri-phonons are given by following simple expressions:

$$E_2 = 2\omega - 2A \quad (4)$$

and

$$E_3 = 3\omega - 6(A + \tilde{A}). \quad (5)$$

Bound multi-phonons are observed only if the following conditions apply

$$|E_2 - 2\omega| > 2\Delta \quad (6)$$

and

$$|E_3 - 3\omega| > 3\Delta \quad (7)$$

where Δ is the width of the one-phonon band. These inequalities are well fulfilled both for $\omega_T(1)$ and $\omega_T(2)$ in our case. The calculated anharmonicity constants are $A = 10.8$ meV and $\tilde{A} = -5.2$ meV for $\omega = \omega_T(1)$, and $A = 24.4$ meV, $\tilde{A} = -12.0$ meV for $\omega = \omega_T(2)$. These latter values are more realistic since we have assumed that $\omega_T(2)$ results from H vibrations along the c -axis (where the H-H interactions are much stronger).

As well as bound multi-phonon states, we may also observe other peaks in the spectrum. These correspond to the creation of 'single phonon plus bound multi-phonon' excitations. They are expected at neutron energy transfers of

$$\epsilon = \omega_T + E_n. \quad (8)$$

Small features (e.g. marked by the arrow on figure 6) are seen at energy $\epsilon \simeq 442$ meV, which is close to $\omega_T(1) + E_2 = 440.7$ meV.

5. Conclusion

The INS spectra of titanium hydride after high pressure treatment were measured. The splitting of the fundamental optic band and the first observations of bi- and tri-phonon excitations in the δ -phase are reported. The existence of these bound phonon states is associated with the strong H-H interactions along the unique axis of the metal hydride lattice.

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