Crystal structure and lattice dynamics of high-pressure scandium trihydride

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Powder samples of hcp $ScH_{2.9}$ and $ScD_{2.9}$ have been synthesized under a 1 GPa pressure of gaseous hydrogen or deuterium and studied at ambient pressure and 95 K by neutron diffraction. A profile analysis of the diffraction patterns indicated a crystal structure with $P6_3/mmc$ symmetry that differs from the structures of hcp trihydrides of yttrium and rare-earth metals by the absence of long-range order in the displacements of hydrogen atoms from high-symmetry positions. The lattice dynamics of scandium trihydride and, for comparison, yttrium trihydride were studied by inelastic neutron scattering at 20 K in the range of energy transfers 4–250 meV. The spectra of optical H vibrations in these two trihydrides proved to be similar, suggesting similar arrangements of hydrogen atoms on a short-range scale.

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I. INTRODUCTION

Scandium is the lightest element of the group III transition metals. Similar to other group III metals—yttrium, lanthanum and most rare earths—scandium forms a fcc dihydride with a fluorite-type crystal structure at hydrogen pressures well below 1 atm.[1] However, while trihydrides of other metals can also be formed at low hydrogen pressures, the synthesis of scandium trihydride requires pressures greater than 0.3 GPa.[2,3] Samples of the high-pressure scandium trihydride are thermally unstable at ambient conditions. A room-temperature x-ray diffraction investigation of a partly decomposed sample showed it to be a mixture of fcc scandium dihydride with $a=4.874$ Å and hcp trihydride with $a=3.380$ Å, $b=6.135$ Å, $c/a=1.815$.[2]

The lattice parameters of scandium trihydride are significantly smaller and its c/a ratio is larger than those of hcp trihydrides of other group III metals. Nonetheless, the values of the atomic volume of scandium trihydride and other trihydrides form a single smooth dependence if plotted as a function of the ionic radius of the metal.[2] This suggests that all these trihydrides belong to the same family and, in particular, the coordination of H atoms in their hcp metal lattices is similar.

The rather complex hydrogen sublattices and hydrogen vibrational spectra of hcp trihydrides of some rare-earth metals and yttrium were studied earlier by neutron scattering techniques (see Refs. 4–6, and references therein). In the present paper, we studied the crystal structures of scandium trihydride and trideuteride by powder neutron diffraction and measured the H vibrational spectra of scandium trihydride and yttrium trihydride by inelastic neutron scattering (INS).

The INS spectrum of yttrium trihydride was measured mostly for comparison. In addition, this new spectrum involved the interval 4–35 meV of the low-energy "lattice" modes never examined earlier for YH_3.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

Bulk ingots of 99.8 wt% pure Sc and 99.9 wt% Y were used as starting materials. Scandium dihydride and dideuteride and yttrium trihydride were synthesized by gas-phase absorption in a Sieverts-type apparatus using hydrogen or deuterium produced by thermal decomposition of TiH_2 or TiD_2, respectively. The composition of the yttrium trihydride thus prepared was determined from the H_2 uptake and proved to be close to YH_3 in agreement with Ref. 4. A room-temperature x-ray diffraction examination (SIEMENS D-500 diffractometer, monochromated Cu $K_{\alpha 1}$ radiation) showed that the YH_3 sample was a single-phase hcp compound with the lattice parameters $a=3.6712(5)$ Å, $c=6.6068(8)$ Å, $c/a=1.7996(4)$.

The scandium dihydride and dideuteride were powdered in an agate mortar and additionally loaded with hydrogen and deuterium, respectively, at a pressure of 1 GPa and a temperature of 250 °C for 24 h. The hydrogenation technique is described elsewhere.[7] The synthesized samples of scandium trihydride and trideuteride were then rapidly cooled under pressure to 150 K, the pressure was released, and the samples were removed from the high-pressure cell, and when not in use, stored in liquid nitrogen to prevent hydrogen/deuterium loss.

Powdered samples of scandium trihydride and trideuteride, each weighing 1.2 g, were studied by neutron diffraction at 95 K with the D1B diffractometer at ILL, Grenoble, using neutrons with wavelengths of $\lambda = 2.53$ and 1.286 Å. The diffractometer was equipped with a position-sensitive detector, covering 80° in 2ϑ with 400 cells of 0.2° width. The sample was placed in a cylindrical, thin-walled vanadium can. The background was determined in a separate empty-can measurement and subtracted from the measured diffraction patterns. The resulting neutron spectra were analyzed using the Rietveld profile refinement technique implemented in the DBWS-9411 computer program.[8]

The same 1.2 g sample of scandium trihydride and a 7 g sample of powdered yttrium trihydride were investigated by INS at 20 K in the range of neutron energy transfers 4–175 and 4–300 meV, respectively, using the NERA-PR multicrystal inverted geometry time-of-flight neutron spectrometer at JINR, Dubna. The sample of scandium trihydride was additionally studied by INS at 10 K in the range of energy transfers 25–250 meV using the IN1-BeF neutron spectrometer installed at the hot source of the high-flux reactor at ILL, Grenoble. In the case of the IN1-BeF spectrometer, the energy lost by the neutrons was calculated by subtracting 3.5 meV, the mean energy of neutrons transmitted through the cooled Be filter, from the incident neutron energy. With both spectrometers, the background spectrum from an empty flat sample holder made of thin aluminium foil was measured separately and then subtracted from the raw INS spectrum of the sample.

III. RESULTS AND DISCUSSION

A. Neutron diffraction

According to earlier neutron diffraction investigations (see Ref. 1, and references therein), hcp trihydrides of rare earths are isostructural with HoH_3. The unit cell of HoH_3, space group $P\bar{3}c1$, is a $(\sqrt{3} \times \sqrt{3})R30°$ expansion of the hcp unit cell in the basal plane.[9] Two-thirds of the H atoms occupy distorted tetrahedral t sites. The remaining one-third of the H atoms occupy trigonal-like sites in or near the metal basal planes, referred to as m sites. The m sites can be considered as resulting from the vertical displacement of octahedral sites toward the metal-defined basal planes.

Powder neutron diffraction studies showed[10–12] that yttrium trihydride also has a $P\bar{3}c1$ structure of the HoH_3 type. On the other hand, recent *ab initio* calculations[13–15] demonstrated that significant features of the electronic band structure[13] and the vibrational spectrum[14,15] of YH_3 cannot be explained if its structural symmetry is $P\bar{3}c1$. Instead, two other structures, $P6_3\ cm$ and $P6_3$, were proposed.[14,15] These new "broken symmetry" structures allow a better explanation of the results of INS[4,6] and also of nuclear magnetic resonance (NMR),[16,17] Raman and IR[18,19] studies of YH_3. All three structures proposed for yttrium trihydride are characterized by correlated placements of H_t and H_m atoms leading to the threefold increase in the parent hcp unit cell.

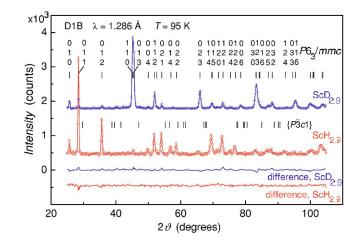Neutron diffraction patterns of scandium trihydride and trideuteride are presented in Figs. 1 and 2. The patterns look

FIG. 1. (Color online) Neutron powder diffraction patterns of $ScH_{2.9}$ and $ScD_{2.9}$ measured at 95 K with the D1B diffractometer at ILL, Grenoble, using neutrons with a wavelength of $\lambda = 1.286$ Å (symbols) and the profile fits calculated with the structure parameters listed in Table I (solid lines) and the differences between the experimental and calculated spectra (two curves at the bottom). The upper row of vertical bars labeled $P6_3/mmc$ shows the positions of diffraction lines calculated for $ScD_{2.9}$. The lower row of bars labeled $\{P\bar{3}c1\}$ shows the positions of superstructure lines, which would be observed in addition to the $P6_3/mmc$ lines (the upper row) if the structure of $ScD_{2.9}$ were of the HoH_3 type.

similar to those of other trihydrides except that they show no signs of long-range hydrogen ordering. As one can see, these patterns mostly consist of lines of the structure with the same $P6_3/mmc$ symmetry and the same lattice parameters as the hcp metal lattice of the scandium trihydride or trideuteride. There are also seen a few weak lines from an admixture of Sc_2O_3 oxide (space group $Ia3$, $a = 9.8672$ Å, the line in Fig.
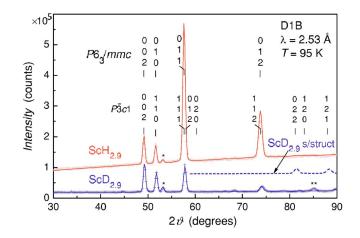

FIG. 2. (Color online) Neutron powder diffraction patterns of $ScH_{2.9}$ and $ScD_{2.9}$ measured at 95 K with the D1B diffractometer at ILL, Grenoble, using neutrons with a wavelength of $\lambda = 2.53$ Å (symbols) and the profile fits calculated with the structure parameters listed in Table I (solid lines). Two rows of vertical bars show the line positions in the diffraction spectra calculated for $ScD_{2.9}$ with the $P6_3/mmc$ structure and the hypothetical $P\bar{3}c1$ structure of the HoH_3 type. The dashed curve shows the calculated profile of superstructure lines of the HoH_3-type structure.

TABLE I. Positional parameters (X, Y, Z), thermal factors (B) and site occupancies (ω) for scandium trihydride and trideuteride according to a Rietveld profile refinement of the neutron diffraction data collected at 95 K with the D1B diffractometer at ILL, Grenoble. R_p and R_{ex} are the obtained and expected profile factors. Hexagonal structure, space group $P6_3/mmc$ (No. 194).

Phase	Atom	Site	X	Y	Z	B (Å^2)	ω
ScH$_x$, $x=2.90(2)$	Sc	$2c$	1/3	2/3	1/4	0.46	1.00
$a=3.373(1)$ Å, $c=6.121(1)$ Å	H$_t$	$4f$	1/3	2/3	−0.088	2.40	0.97
$c/a=1.815(1)$; $R_p/R_{ex}=4.5/4.1$	H$_m$	$4e$	0	0	0.210	1.50	0.48
ScD$_x$, $x=2.87(2)$	Sc	$2c$	1/3	2/3	1/4	0.46	1.00
$a=3.361(1)$ Å, $c=6.101(1)$ Å	D$_t$	$4f$	1/3	2/3	−0.088	2.10	0.97
$c/a=1.815(1)$; $R_p/R_{ex}=6.7/4.6$	D$_m$	$4e$	0	0	0.210	1.40	0.465

2 is marked with an asterisk) and from an unidentified phase (presumably, hydroxide; its line in Fig. 2 is marked with two asterisks). However, any "superstructure" lines resulting from ordering of H$_m$ atoms in the $P\bar{3}c1$, $P6_3 cm$ or $P6_3$ structure are missing. To illustrate the absence of additional lines due to the HoH$_3$-type $P\bar{3}c1$ structure, hypothetical positions of these lines in the diffraction pattern of scandium trideuteride are indicated in Fig. 1 by the row of vertical bars labeled $\{P\bar{3}c1\}$, and hypothetical profiles of the two most intense superstructure lines (202) and (211) are shown in Fig. 2 by the dashed curve.

Profile analysis of the neutron diffraction patterns of scandium trihydride and trideuteride constrained to the $P6_3/mmc$ symmetry produced results presented in Tables I and II. The quality of the refinement is illustrated by the difference spectra at the bottom of Fig. 1. The resulting unit cell is schematically shown in Fig. 3.

As seen from Table I, the profile refinement yields the compositions of the samples close to ScH$_{2.9}$ and ScD$_{2.9}$. The ScH$_{2.9}$ composition agrees with the earlier estimate H/Sc ≥ 2.8 for samples of scandium trihydride synthesized under similar conditions.[2]

The structures of ScH$_{2.9}$ and ScD$_{2.9}$ are identical. The vertical displacements $\Delta z=0.210 \cdot c \approx 1.3$ Å of hydrogen m sites from the ideal octahedral positions $(0,0,0)$ are of the same order of magnitude as in HoH$_3$, but in contrast to the case of HoH$_3$ these displacements are all equal. As a result, the m sites form dumbbells centered at the Sc-defined basal planes and oriented along the c axis. Because of the small distance $2\ell=2 \cdot (1/4-0.210) \cdot =0.08 \cdot c \approx 0.5$ Å between the sites in a dumbbell, these positions cannot be occupied by hydrogen simultaneously due to the "blocking effect"[20] requiring that the distance between hydrogen atoms in a metal should not be significantly less than 2 Å. Only a half of the m sites are therefore accessible for hydrogen atoms. The occupancies $\omega=0.48$ and 0.465 of m sites in ScH$_{2.9}$ and ScD$_{2.9}$ (Table I, the last column) agree with this constraint and suggest a random distribution of H or D atoms over these sites in accordance with the $P6_3/mmc$ symmetry of the structure.

The H$_t$ atoms are displaced along the c axis from the ideal positions with $Z_{id}=-\frac{1}{3}(a/c)^2 \approx -0.101$ away from the basal planes. The displacement $\Delta z=(Z-Z_{id}) \cdot c \approx (-0.088 +0.101) \cdot \approx 0.013 \cdot c \approx 0.08$ Å leads to the increase in the distance between the nearest H$_t$ atoms from 1.82 to 1.98 Å and between the nearest H$_m$ and H$_t$ atoms from 2.04 to 2.09 Å. These distances exceed the blocking value of about 2 Å and hydrogen can therefore occupy every H$_t$ site regardless of the occupancy of the nearest H$_m$ site, which is, in fact, observed ($\omega_t \approx 1$, see Table I).

Assuming the $P6_3/mmc$ symmetry of the structure of scandium trihydride, the profile analysis thus gives a noncontradictory interpretation of the neutron diffraction data. However, the B factors for hydrogen atoms and especially those for t-hydrogen atoms (see Table I) are too large to be of purely dynamic origin. This suggests the occurrence of significant static displacements of hydrogen atoms away from the calculated positions.

B. Inelastic neutron scattering

Figure 4 shows the INS spectra $S(Q, \omega)$ of the ScH$_{2.9}$ powder. The sample was first measured for two days with the

TABLE II. Interatomic distances in ScH$_{2.9}$ (in angstroms).

Sc-H$_t$	Sc-H$_m$	H$_t$-H$_t$	H$_t$-H$_m$	H$_m$-H$_m$
2.185; 2.069	1.961	1.983	2.09	2.57

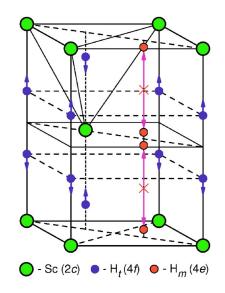◯ - Sc (2c) ● - H$_t$ (4f) ◯ - H$_m$ (4e)

FIG. 3. (Color online) The hexagonal unit cell of scandium trihydride, space group $P6_3/mmc$. The arrows show the vertical displacements of hydrogen atoms from the ideal tetrahedral positions (solid circles) and from the ideal octahedral positions (crosses).
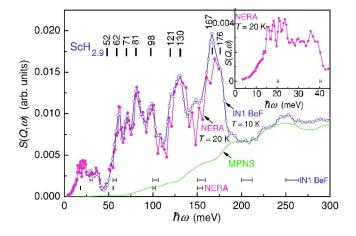
FIG. 4. (Color online) The dynamical structure factor $S(Q,\omega)$ of $ScH_{2.9}$ powder as a function of the energy loss $\hbar\omega$ of the inelastically scattered neutrons. The horizontal bars show the energy resolution, respectively, of the two neutron spectrometers used, NERA-PR (JINR, Dubna) and IN1-BeF (ILL, Grenoble). The lower thin solid line labeled "MPNS" presents the estimated multiphonon neutron scattering contribution.
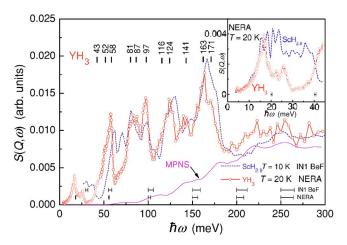

FIG. 5. (Color online) The dynamical structure factor $S(Q,\omega)$ of $ScH_{2.9}$ and YH_3 powders as a function of the energy loss $\hbar\omega$ of the inelastically scattered neutrons. The horizontal bars show the energy resolution. The lower thin solid line presents the estimated multiphonon contribution.

high-resolution NERA-PR spectrometer at $T=20$ K in the range of neutron energy transfers starting from 4 meV. However, the mass 1.2 g of the sample was insufficient to get a spectrum with good statistics at neutron energies exceeding 100 meV, and the same $ScH_{2.9}$ sample was additionally measured for 4 h with the high-luminosity IN1-BeF spectrometer at $T=10$ K in the energy range 25–300 meV.

As seen from Fig. 4, the two spectra agree with each other. The spectrum measured with the NERA-PR spectrometer is preferable at energies below 80 meV due to its better resolution, whereas the spectrum measured with IN1-BeF is more reliable at energies above 80 meV because of the better statistical accuracy. The vertical bars in the upper part of Fig. 4 indicate positions of the scattering maxima with due regard to this preference.

Figure 5 shows the INS spectrum $S(Q,\omega)$ of a 7 g powder sample of YH_3 measured for one day with the NERA-PR spectrometer. This spectrum includes the ranges of lattice modes ($\hbar\omega<30$ meV) and optical H vibrations ($\hbar\omega>40$ meV). The optical part of the spectrum coincides well with the spectrum of YH_3 from Ref. 4 measured at $\hbar\omega>35$ meV.

As seen from the inset to Fig. 5, the low-energy part of the vibrational spectrum of YH_3, which is mainly determined by vibrations of the Y atoms, extends up to about 29 meV and shows features at 14.8, 16.8, 19.5, 22.8, and 25.8 meV. The low-energy part of the INS spectrum of $ScH_{2.9}$ stretches to approximately 41 meV and demonstrates a more complex intensity distribution with peaks at 15.5, 18.3, 21.0, 23.8, 27.0, 30.0 and 36.0 meV. The ratio $41/30\approx1.41$ of the high-energy cutoffs of the lattice modes in YH_3 and $ScH_{2.9}$ is close to the mass ratio $\sqrt{m_Y/m_{Sc}}\approx1.41$, which points to nearly the same values of the Sc-Sc and Y-Y force constants in these trihydrides.

As one can see from Fig. 5, the INS spectra of $ScH_{2.9}$ and YH_3 are similar in the range $\hbar\omega>40$ meV of optical H vi-

brations. Most peaks in the spectrum of $ScH_{2.9}$ are just shifted to higher energies due to the shorter hydrogen-metal distances and correspondingly stronger hydrogen-metal bonding.

Discussing the optical vibrations in hydrides, however, it is usually more convenient to consider one-phonon INS spectra because they better reproduce the phonon density of states. The one-phonon spectra of $ScH_{2.9}$ and YH_3 are shown in Fig. 6. These spectra are obtained from the experimental INS spectra by subtracting the contributions from the multiphonon neutron scattering (lower thin solid lines in Figs. 4 and 5, respectively) estimated in a harmonic isotropic approximation using the iterative technique of Ref. 21.

As seen from Fig. 6, the one-phonon spectrum of $ScH_{2.9}$ reproduces every main feature of the YH_3 spectrum in the range of the fundamental optical band from about 40 to 180 meV except the interval 60–75 meV, where the spectrum of $ScH_{2.9}$ clearly shows additional intensity. Nevertheless, this difference can also be considered insignificant because of the anomalously high sensitivity of the optical H spectra of trihydrides to small changes in the arrangement of H atoms. By way of illustration, Fig. 7 shows the spectra for YH_3 calculated in Ref. 15 assuming the $P\bar{3}c1$, $P6_3cm$ and $P6_3$ structure. These structures differ in the magnitudes and directions of displacements of H atoms from symmetrical positions in the hcp metal lattice. The differences are small and the three structures can only be distinguished from each other in very sophisticated neutron diffraction experiments using specially prepared, nearly single-crystalline samples.[6] Meanwhile, as seen from Fig. 7, the calculated optical H spectra of these very similar structures differ drastically.

The difference between the INS spectra of $ScH_{2.9}$ and YH_3 at energies from 60 to 75 meV (Figs. 5 and 6) is much smaller than the variation of the calculated vibrational intensity of YH_3 in this energy interval and adjacent regions caused by subtle changes in the arrangement of H atoms in the $P\bar{3}c1$, $P6_3cm$ and $P6_3$ structures (Fig. 7). One could therefore expect that the difference in the arrangements of H
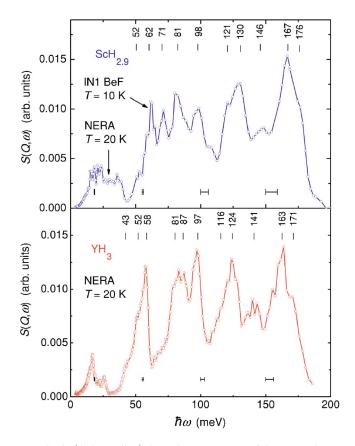
FIG. 6. (Color online) One-phonon spectra of $ScH_{2.9}$ and YH_3 obtained from the experimental INS spectra by subtracting the contributions from the multiphonon neutron scattering shown in Figs. 4 and 5, respectively, by the lower thin solid lines.

FIG. 7. (Color online) One-phonon INS spectrum of YH_3 (present paper) and total phonon densities of states calculated for YH_3 in the $P\bar{3}c1$, $P6_3cm$ and $P6_3$ structure (Ref. 15).

atoms in $ScH_{2.9}$ and YH_3 is even less than in those three virtually indistinguishable crystal structures proposed for YH_3.

This implies, in particular, that the displacements of H_m atoms from the basal metal planes in $ScH_{2.9}$ are not all equal and should be correlated as in YH_3. At the same time, inasmuch as inelastic neutron scattering is mostly sensitive to the local environment of the scattering atom, these correlations in $ScH_{2.9}$ may show no long-range order. The occurrence of large hydrogen displacements, either chaotic or correlated on a short-range scale, is consistent with our neutron diffraction results and explains the large values of B factors for hydrogen atoms (Table I).

One can speculate that the local symmetry of hydrogen arrangements in other hcp trihydrides is also lower than the long-range symmetry determined by such methods as neutron diffraction. This would explain, for example, why the "local" properties of YH_3 measured by NMR,[16,17] INS,[4,6] Raman and IR[18,19] spectroscopy are better described with the $P6_3cm$ or $P6_3$ structure[14,15] than with the higher symmetry $P\bar{3}c1$ structure established[10–12] by powder neutron diffraction.

The occurrence of large hydrogen displacements correlated in a similar manner in all hcp trihydrides of the group III metals also explains why the spectrum of optical H vibrations in lutetium trihydride is similar to those in other rare-earth trihydrides, while the crystal structure of LuH_3 is more
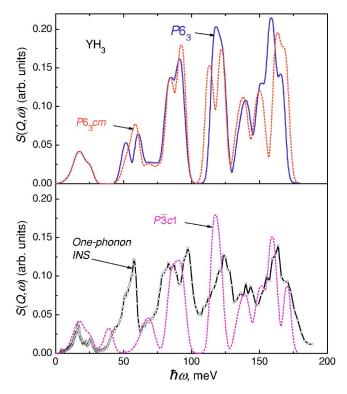
symmetrical according to the neutron diffraction data (LuH_3 was studied by INS[4] and LuD_3 was studied by powder neutron diffraction[4] and NMR[22]). Interestingly, the structure of LuH_3 is similar to the $P6_3/mmc$ structure of scandium trihydride and the presence of minor diffraction features only points to a more complex arrangement of hydrogen atoms.[22] Lutetium trihydride has smaller lattice parameters than hcp trihydrides of other rare-earth metals and yttrium, and the parameters of scandium trihydride are smaller than those of lutetium trihydride. Therefore, there seems to be a tendency towards the increase in the long-range symmetry of the crystal structure of hcp trihydrides of the group III metals with decreasing atomic volume. The spectrum of H vibrations is likely to vary monotonically, too. In particular, the additional scattering intensity in the range 60–75 meV that makes the INS spectrum of $ScH_{2.9}$ slightly different from that of YH_3 (see Figs. 5 and 6) is also observed only in the spectrum of LuH_3.

The similarity between the spectra of optical H vibrations in $ScH_{2.9}$ and YH_3 makes it possible to assign some portions of the $ScH_{2.9}$ spectrum to certain modes of H vibrations using the phonon density of states[14,15] calculated for YH_3. Namely, the H_m vibrations polarized along the c axis have frequencies between 45 and 110 meV, whereas the ab-polarized vibrations of H_m atoms have frequencies around 170 meV. The frequencies of the ab-polarized vibrations of H_t atoms lie in the interval 75–140 meV and those of the c-polarized vibrations in the interval 140–170 meV.

IV. CONCLUSIONS

The INS investigation has shown that the spectrum of hydrogen vibrations in $ScH_{2.9}$ is rather complex and its optical part has much in common with the spectra of hcp trihydrides of other group III metals, yttrium and rare earths. This suggests that the local environments of H atoms in $ScH_{2.9}$ are similar to those in other hcp trihydrides characterized by large and correlated displacements of H atoms from symmetrical positions.

At the same time, the neutron diffraction investigation of $ScH_{2.9}$ and $ScD_{2.9}$ revealed no long-range order in the H or D displacements and demonstrated that the crystal structure of scandium trihydride has a higher symmetry, $P6_3/mmc$, than the structures of other hcp trihydrides. Inasmuch as INS is mostly sensitive to the local environment of the light atom,

the results of the neutron diffraction and INS investigation of scandium trihydride can be reconciled by assuming that hydrogen displacements characteristic of other trihydrides do occur in this compound, but they are not correlated on a long-range scale. This assumption also explains the large values of the Debye–Waller factors obtained for hydrogen atoms in scandium trihydride while modelling the neutron diffraction data with the $P6_3/mmc$ structure.

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