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Raman scattering by phonons and crystal-field excitations in cerium hydrides

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ABSTRACT

The effect of cerium hydrides (deutrides) stoichiometry, $CeH(D)_{2+x}$ ($x = 0–0.90$), on the vibrational and Ce^{+3} crystal-field excitations was studied at room temperature by means of Raman scattering spectroscopy. The assignment of CeH_{2+x} vibrational Raman bands, with $x < 0.6$, are facilitated by the remarkable similarity of their frequencies to the previously measured inelastic neutron scattering (INS) frequencies for the corresponding LaH_{2+x}. Above $x \approx 0.60$ the INS and Raman spectra become increasingly different presumably due to the repulsive H–H interactions, which are also known to increase the magnitude of dispersion in optic-mode vibrations. The intensity of a band at ~810 cm^{-1} relative to that of a band at ~710 cm^{-1} decreases by an order of magnitude from $x \approx 0.60$ to $x \approx 0.72$ and remain practically constant up to $x = 0.90$. Since at room temperature the composition dependent structural tetragonal-cubic and electronic metal-semiconductor transitions occur at $x \approx 0.60$ and $0.7 < x < 0.8$, respectively, the above spectral changes cannot be clearly assigned to either.

1. Introduction

Cerium forms a wide range of non-stoichiometric hydrides CeH_{2+x} ($0 \leq x \leq 1$) when it reacts with hydrogen [1]. This system is characterized by various electronic and structural transitions, which are both composition and temperature dependent.

At room temperature (RT), the dihydride ($x = 0$) has the fluorite structure in which the hydrogens almost fully occupy the tetrahedral interstitial sites (H_t) [2]. Increasing the hydrogen content results in octahedral sites (H_o) occupation, during which various crystallographic structures are identified. The onset of tetragonal distortion has been detected at $x \approx 0.15$, and up to $x \approx 0.45$ a complete tetragonality is maintained [3]. At higher x, a minor cubic phase appears, and at $x \approx 0.6$ the hydride becomes entirely cubic with random hydrogen occupation of the octahedral sites of the fcc lattice. Finally, the trihydride attains the BiF_3-type structure [2] (see Fig. 1).

The electronic properties of cerium hydride are affected by both stoichiometry and temperature: At the temperature range of 160–300 K, CeH_{2+x}, $x < 0.70$, is metallic, whereas for $x > 0.80$ the hydride is semiconductor and for $x \to 1$ an insulator. At room temperature, the hydrides' resistivity gradually increases up to $x \approx 0.75$, whereas at $x > 0.75$ the increase becomes much steeper. Hence, around $x \approx 0.75$ a metal–semiconductor (MS) transition occurs [4]. Upon temperature decrease, CeH_{2+x}, $0.70 < x < 0.80$, undergoes MS transition at ~245 K, which is accompanied by cubic–tetragonal (CT) phase transition [5,6].

Order–disorder transition within the octahedral interstices, which gives rise to a tetragonal distortion of the cubic unit cell, was the proposed mechanism for the MS transition in the CeH_{2+x} ($0.7 < x < 0.8$); breakdown of the octahedral vacancy lattice leads to a breakdown of a delocalized carrier band, which is believed to drive the MS transition [5–8].

In a series of papers [9–11], Fujimori et al. explored the manifestation of the cerium hydride's electronic and structural properties in the Raman scattering by phonons. They suggested for various hydride compositions different super-cell structures and assigned their corresponding Brillouin zone (BZ) center ($k = 0$) vibrational modes, which were obtained by standard group-theoretical analysis. Frequency variations in the Raman spectra have been explained by a model which considers softening of the H_t ions phonon mode, which is enhanced with an increase in x [9]. This softening has been attributed to variations in electronic-screening that strongly affects the electron–phonon interaction.

Tetrahedral hydrogen ions are almost fully occupied at $x \geq 0$ [2], and are practically arranged with long-range order. Since this is definitely not the case for the octahedral H-sublattice at $x > 0.6$ [7,8], hydrides in these stoichiometries are considered order–disorder type of crystal with two intermixed (H_t and H_o) sublattices [12,13]. Absence of long-range order in the H_o sublattice precludes the assignment of the Raman bands to Z center phonons exclusively, as suggested in Ref. [9], and therefore calls for a re-examination of the Raman spectral analysis of cerium hydrides.

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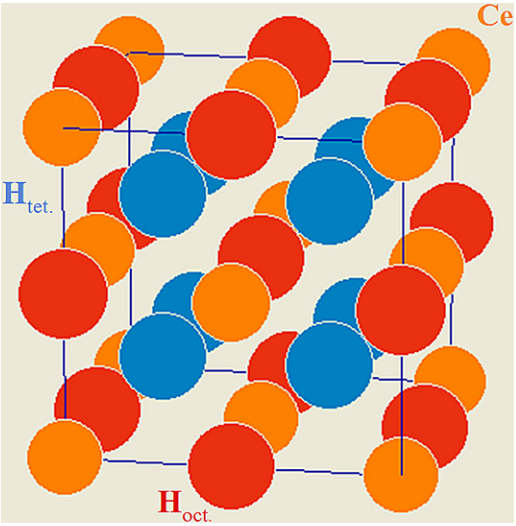

Fig. 1. The BiF_3-type structure of CeH_3. Removal of the H_o sublattice will result in the cubic CaF_2-type structure of CeH_2.

In Ce^{+3} ion, the spin-orbit interaction splits the lowest energy configuration ($4f^1$) into two multiplets, $^2F_{5/2}$ and $^2F_{7/2}$, separated by about 2300 cm^{-1} [14]. The crystal-field (CF) further splits these multiplets depending on its symmetry and on the strength of its interaction. Unlike the CF excitations among the $^2F_{5/2}$ lower multiple of Ce^{+3} ion in cerium hydrides (deutrides), which had been previously studied by means of inelastic neutron scattering (INS) [15,16] and Raman spectroscopy [17], the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ intermultiplet scheme is yet unexplored.

In this paper we present a room temperature Raman study, which was carried out for $CeH(D)_{2+x}$ ($x = 0$–0.90), in order to clarify the effect of hydride (deuteride) stoichiometry on the vibrational and Ce^{+3} electronic Raman scattering. Some remarkable correlations between our CeH_{2+x} Raman data and previously published INS data for the corresponding LaH_{2+x} [18–23] are elucidated and used for the purpose of spectral interpretation of the various vibrational bands.

2. Experimental section

$CeH(D)_{2+x}$ powders in the composition range of $0 \le x \le 0.90$, with $\Delta x \approx \pm 0.02$ were prepared by exposing cerium metal samples (99.9% purity) to hydrogen (deuterium). Prior to their exposure the samples were mechanically polished, immersed in ethanol and placed under a vacuum atmosphere. After a few purging cycles they were heated to ~400 °C, in order to remove the residual hydroxide impurities and crack the native oxide layer, and then exposed to hydrogen at ~340 °C. In order to achieve optimal hydride homogeneity few decomposition–hydridization cycles were performed.

Hydride samples, which were capsulated under inert atmosphere, were placed under a Renishaw Raman microscope, using the 633 nm line of a He–Ne laser for excitation. The observed colors of the various hydrides were found to be consistent with the previous reports [24–26]. XRD which were obtained from $CeH_{2.00}$ and $CeH_{2.80}$ were in very good agreement with previous studies [24].

3. Results and discussions

3.1. Vibrational Raman scattering of $CeH(D)_{2+x}$

Fig. 2 presents the RT Raman spectra of $CeH(D)_{2+x}$, $0 \le x \le 0.90$ in the range of 400–1400 cm^{-1}. The composition ranges for the major cubic/tetragonal structures [3] are also shown. In order to correct for the mass difference, under the assumption of a harmonic potential, the cerium deutrides spectra are plotted at energies scaled by $\omega_H/\omega_D \approx \sqrt{m_D/m_H} = \sqrt{2}$. The intensities of the various spectra are also scaled to make the results comparable.

No distinguishable Raman signal has been detected for the metallic $CeH_{2.00}$, owing to the low penetration depth of visible light, which results from the screening by the free carriers. For $CeH(D)_{2.30}$, a clear signal has been detected. Previous attempt to measure the Raman spectrum from cerium hydride with slightly higher composition ($CeH_{2.33}$) has not been successful [9], presumably due to the lower measurement sensitivity. Excluding the above discrepancy, our results are in good agreement with those reported in Ref. [9] for similar hydride compositions.

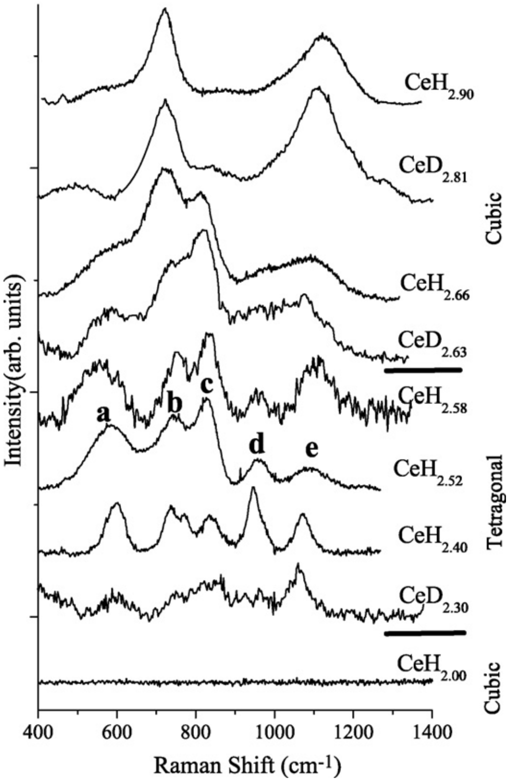

Fig. 2. Raman spectra of $CeH(D)_{2+x}$, $0 \le x \le 0.90$. Cerium deutrides spectra had been plotted at energies scaled by $\sqrt{2}$. For the $CeD_{2.81}$ spectrum a weak CeO_2 signal was removed for clarity.

Around $x \approx 0.6$–0.7 a sharp increase in the Raman scattering intensities of the various bands is observed (not shown). This increase is attributed to changes in the dielectric and structural properties of the hydride around this composition [4,6]. Fig. 3 compares the Raman spectra of $CeH_{2.40}$ and $CeD_{2.40}$ with the latter being plotted at energies scaled by $\sqrt{2}$. The intensities were also scaled to make the results comparable. The ratio between the energies of the H and D vibrational peaks is slightly lower than the harmonic value, and the isotope shift is 1.38–1.39. Comparison between the Raman spectra of higher x shows similar isotope shifts. This result indicates a small anharmonicity in the H potential, which appears for all phonons throughout the entire investigated hydride stoichiometry range. Similar deviation from the harmonic value of $\sqrt{2}$ has also been detected for $LaH_{2.50}$ by INS [18]. For ZrH_2 a 1.35 isotope shift points at a stronger deviation from harmonicity [27].

3.1.1. Raman scattering of CeH_{2+x} vs. INS of LaH_{2+x}

It is well known that the structural properties in La–H and Ce–H systems are very similar [25]. Recent extensive INS [18–20] and neutron powder diffraction (NPD) [21–23] studies by Udovic et al., significantly improved the understanding of the vibrational and structural properties of the La–H system. We may therefore investigate the phonon characteristics of the cerium hydride system by correlating our Raman spectra with INS spectra of the corresponding lanthanum hydrides, which are briefly summarized below.