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Distortion of the fcc lattice in superstoichiometric β-$YH_{2+\delta}$ and cubic $YH_{3-\eta}$ thin films

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Abstract

We have monitored with Raman spectroscopy the metal insulator transition of Y films grown on (1 1 1) CaF_2 substrates and capped with Pd. Characteristic for the γ phase is a Raman spectrum with nine lines at room temperature. In the stoichiometric β phase, YH_2 shows only one line. In the superstoichiometric β phase of $YH_{2+\delta}$ we find changes in the spectra which are not compatible with a cubic lattice. The Raman mapping image during unloading of a Y film shows a regime of coexistence between the γ and the superstoichiometric β phase. The results are compared with measurements on $Mg_{0.1}Y_{0.9}H_x$ which also show a distortion of the cubic lattice.

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Keywords: Thin films; Crystal structure and symmetry; Inelastic light scattering

1. Introduction and theory

The optical properties of yttrium hydride films show important changes with hydrogen content [1]: the dihydride (YH_2) is a shiny metal while the trihydride (YH_3) is an insulator transparent in a large part of the visible spectrum. The metal-insulator transition (MIT) is accompanied by a structural phase transition, from cubic YH_2 to hexagonal YH_3 [2]. For hydrogen concentrations $1.8 \leq x \leq 2.1$ the yttrium atoms are arranged in a face centered cubic (fcc) lattice, with hydrogen fully occupying the tetrahedral (H_t) interstices at $x = 2.0$. This is called the β phase. Above $x = 2.0$ the excess hydrogen atoms partially occupy the octahedral (H_o) interstices. In bulk material [3–7] and in thin films [8] an ordering of the hydrogen sublattice was observed in superstoichiometric $YH_{2+\delta}$ with $\delta < 0.1$, driving the cubic lattice to a tetragonal distortion. If the hydrogen content is higher than $x = 2.1$ a structural change to a hexagonal close packed (hcp) γ phase occurs. van der Molen et al. [9] showed that the fcc structure can be stabilized in $YH_{3-\eta}$ by alloying Y with Mg prior to hydrogenation. This cubic $YH_{3-\eta}$ was shown to be an insulator with a gap comparable to that of hcp YH_3. In this paper, we focus on the first-order Raman scattering by phonons in thin films of YH_x and $Mg_{0.1}Y_{0.9}H_x$ with hydrogen concentrations around the MIT.

The theoretical background necessary for the interpretation of the experimental data includes a standard group-theoretical analysis of the crystal structures involved in the phase transition [10]. Table 1 collects the results of the calculation. For hcp YH_3 we use the $P6_3cm$ structure. This is the most favored structure from Raman spectroscopy [11], [12] and neutron diffraction measurements [13], which also agrees with theory [14]. In agreement with neutron diffraction [3] and theory [5] we assume for the superstoichiometric $YH_{2+\delta}$ the $I4/mmm$ crystal structure. For fcc YH_3 the proposed structure is the BiF_3 [15] type in the $Fm\bar{3}m$ space group, in which all the tetrahedral and the octahedral sites are occupied by H atoms. For YH_2 and fcc YH_3 only one phonon is Raman active, a triply degenerated F_{2g} vibration of the

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Table 1
Results of the FGA for YH_2, $YH_{2+\delta}$ and YH_3

Material	Raman active modes	H_o modes
YH_2 fcc	F_{2g}	–
$YH_{2+\delta}$	$3A_{1g} + 3B_{1g} + B_{2g} + 5E_g$	$B_{1g} + E_g$
YH_3 hcp	$7A_1$+$11E_1$+$12E_2$	$2A_1$+$3E_2$+$3E_1$
YH_3 fcc	F_{2g}	–

Material	H_t modes	Y modes
YH_2 fcc	F_{2g}	–
$YH_{2+\delta}$	$2A_{1g} + 2B_{1g} + B_{2g} + 3E_g$	$A_{1g} + E_g$
YH_3 hcp	$4A_1$+$6E_2$+$3E_1$	$2A_1$+$3E_2$+$3E_1$
YH_3 fcc	F_{2g}	–

tetrahedral hydrogen atoms. In the tetragonal $YH_{2+\delta}$ two vibrations of the metal atoms are Raman active, having A_{1g} and E_g symmetry. In addition the FGA predicts 10 vibrations due to hydrogen in octahedral and tetrahedral positions. The hcp YH_3 presents 8 vibrations of the Y atoms and 22 vibrations of the hydrogen atoms from different positions.

2. Experimental procedure

The yttrium samples have been grown by molecular-beam epitaxy on (1 1 1) CaF_2 substrates. The base pressure during the deposition was lower than 1×10^{-9} mbar. The quality of the yttrium film was monitored in situ by reflection high energy electron diffraction (RHEED). The RHEED patterns showed sharp streaks, Kikuchi lines and Laue circles evidencing the high crystallinity of the yttrium layer [16]. To protect the yttrium films against oxidation and to support the hydrogenation process, the films were covered with 10 nm thick Pd layers which were deposited at room temperature. The samples were loaded at room temperature in a gas cell with 99.999% pure H_2 at a pressure of 1 bar.

The $Mg_{0.1}Y_{0.9}$ samples are prepared by coevaporation of Y and Mg on CaF_2 substrates and are covered with a thin Pd layer as described in Ref. [9].

Raman spectra have been recorded using a commercial micro-Raman spectrometer (Jobin Yvon LabRam HR), operated with a notch filter and a grating monochromator. The excitation radiation is the 532 nm wavelength line of a diode-pumped Nd:YAG laser of 150 mW, focused on an area of a few μm^2.

For the Raman mapping we used a motorized *xy* microscope stage. A certain surface of the sample is scanned in equal steps of 10 μm. For each position, a Raman spectrum is recorded. In the map, the distribution of different phases in the sample is illustrated with different gray levels.

3. Results and discussion

The Raman spectra presented in Fig. 1 illustrate the unloading process of a thin Y film capped with Pd. The Raman measurements are performed through the CaF_2 substrate which gives the main feature in all the spectra at 322 cm^{-1}. For clarity, the various spectra in all the figures are displaced, adding a constant term to the intensity.

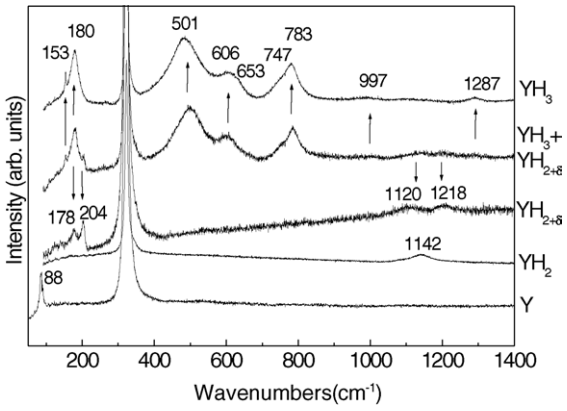

Fig. 1. The switching process monitored with Raman spectroscopy.

The Raman spectrum of a metallic Y film is presented at the bottom of Fig. 1. The single, two-fold degenerate line of yttrium is visible at 88 cm^{-1} [17]. After loading the film in 1 bar hydrogen atmosphere, the spectrum shows in the YH_3 phase the typical shape, with nine lines, at room temperature (top curve in Fig. 1). Subsequently, the spectra in Fig. 1 represent (from top to bottom): a mixture between YH_3 and $YH_{2+\delta}$, $YH_{2+\delta}$ and YH_2. The energies of the Raman lines are attached to the spectra.

We are particularly interested to know how the $YH_{2+\delta}$ phase is starting to form from the YH_3 phase during unloading of the film. The picture in Fig. 2 shows a Raman map of the surface of a yttrium hydride film during unloading. The gray steps in the picture represent the intensity ratio between the line at 204 cm^{-1} of $YH_{2+\delta}$ and the line at 153 cm^{-1} of YH_2 (see Fig. 1). Bright regions correspond to a domination of the $YH_{2+\delta}$ phase, while the dark regions indicate the presence of the YH_3 phase. We observe that the tetragonal structure starts to form as small domains which become bigger when

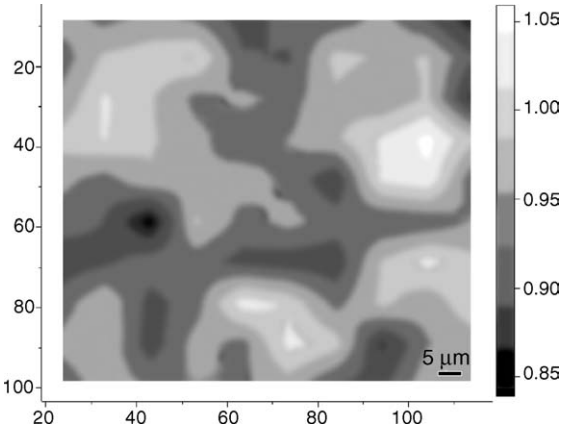

Fig. 2. Raman mapping for a YH_x surface during unloading.

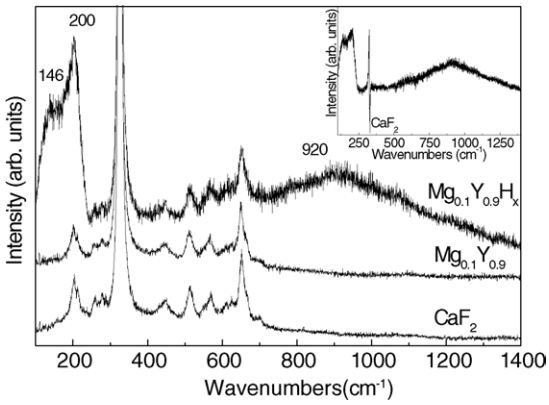

Fig. 3. Raman spectra of metallic $Mg_{0.1}Y_{0.9}$ and insulating $Mg_{0.1}Y_{0.9}H_x$, x=3 − η.

the sample unloads. This resembles the pixel switching of YH_x described by Kerssemakers et al. [18], with the mention that the phases involved are the hcp YH_3 and the tetragonal $YH_{2+\delta}$.

The detection of the tetragonal $YH_{2+\delta}$ phase brought us to search for distortions during the loading of metal hydride systems which are cubic in the dihydride and the trihydride phase. A good candidate is fcc $YH_{3-\eta}$ stabilized by MgH_2. van der Molen et al. [9] have evidenced with X-ray diffraction analysis of Mg_zY_{1-z} films after hydrogenation a transition from hcp YH_3 to fcc YH_3 for Mg contents above $z = 0.10$. Raman measurements for films with the Mg content $z = 0.10$ show similarities to the spectra of $YH_{2+\delta}$. The spectra in Fig. 3 are different from those for hcp YH_3 since the Mg content is high enough to stabilize the cubic YH_3 structure. The spectra observed in Fig. 3 represent (from bottom to top) CaF_2 substrate, metallic $Mg_{0.1}Y_{0.9}$ and hydrogenated $Mg_{0.1}Y_{0.9}$. The substrate gives, besides the line at 322 cm^{-1} some other peaks, which are easy to identify in all the spectra. In the inset of Fig. 3, the substrate spectrum has been subtracted from the hydride spectrum. The measurement is not compatible with the factor group analysis for the ideal cubic YH_3 in the BiF_3 crystal structure (see Table 1). The three observed lines are more than predicted for this structure indicating a lowering of the symmetry like a tetragonal distortion. This is reminiscent of the isostructural system LaH_3 in which a transition from cubic to a tetragonal structure as a function of the temperature has been observed in X-ray diffraction and specific heat measurements [19] and [20].

4. Summary

We have cleared up the picture of the switching of an yttrium film adding the $YH_{2+\delta}$ tetragonal phase between hcp YH_3 and fcc YH_2. This phase is clearly observed during the unloading of the film. Raman mapping shows a regime of coexistence of $YH_{2+\delta}$ and hexagonal YH_3. The number of the Raman lines in the tetragonal $YH_{2+\delta}$ is compatible with the factor group analysis for the $I4/mmm$ structure. Measurements on $Mg_{0.1}Y_{0.9}H_x$ samples show interesting similarities with the $YH_{2+\delta}$ spectra. Moreover, the number of the Raman peaks in $Mg_{0.1}Y_{0.9}H_x$ is higher than predicted by the factor group analysis, pointing to a lowering of the symmetry from the proposed BiF_3 structure.

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References

[1] J.N. Huiberts, R. Griessen, J.H. Rector, R.J. Wijngaarden, J.P. Dekker, D.G. de Groot, N.J. Koeman, Nature (London) 380 (1996) 225.
[2] M. Kremers, N.J. Koeman, R. Griessen, P.H.L. Notten, R. Tolboom, P.J. Kelly, P.A. Duine, Phys. Rev. B 57 (1998) 4943.
[3] T.J. Udovic, J.J. Rush, I.S. Anderson, J. Alloys Compd. (1995) 231; T.J. Udovic, Q. Huang, J.J. Rush, J. Schefer, I.S. Anderson, Phys. Rev. B 51 (1995) 12116.
[4] P. Vajda, J.N. Daou, Phys. Rev. Lett. 66 (1991) 3176; J.N. Daou, P. Vajda, Phys. Rev. B 45 (1992) 10907.
[5] Y. Wang, M.Y. Chou, Phys. Rev. B 49 (1994) 10731; S.N. Sun, Y. Wang, M.Y. Chou, Phys. Rev. B 49 (1994) 6481.
[6] X. Helluy, J. Kümmerlen, A. Sebald, O.J. Zogal, Solid State NMR 14 (1999) 225–230.
[7] O.J. Zogal, A.H. Vuorimäki, E.E. Ylinen, Eur. Phys. J. B 10 (1999) 201–207.
[8] A.-M. Carsteanu, M. Rode, D. Zur, A. Borgschulte, H. Schröter, J. Schoenes, Phys. Rev. B 69 (2004) 134102.
[9] S.J. van der Molen, D.G. Nagengast, A.T.M. van Gogh, J. Kalkman, E.S. Kooij, J.H. Rector, R. Griessen, Phys. Rev. B 63 (2001) 235116.
[10] H. Kuzmany, Solid State Spectroscopy, Springer-Verlag, Berlin, 1989.
[11] H. Kierey, M. Rode, A. Jacob, A. Borgschulte, J. Schoenes, Phys. Rev. B 63 (2001) 134109.
[12] J. Schoenes, A. Borgschulte, A.-M. Carsteanu, H. Kierey, M. Rode, J. Alloys Compd. 356–357 (2003) 211.
[13] T.J. Udovic, Q. Huang, R.W. Erwin, B. Hjövarsson, R.C.C. Ward, Phys. Rev. B 61 (2000) 12701.
[14] P. van Gelderen, P.J. Kelly, G. Brocks, Phys. Rev. B 68 (2003) 094302.
[15] T. Miyake, F. Aryasetiawan, H. Kino, K. Terakura, Phys. Rev. B 61 (2000) 16491.
[16] A. Jacob, A. Borgschulte, J. Schoenes, Thin Solid Films 414 (2002) 39–42; A. Borgschulte, S. Weber, J. Schoenes, Appl. Phys. Lett. 82 (2003) 2898.
[17] R.T. Demers, S. Kong, M.V. Klein, R. Du, C.P. Flynn, Phys. Rev. B 16 (1988) 11523.
[18] J.W.J. Kerssemakers, S.J. van der Molen, N.J. Koeman, R. Günther, R. Griessen, Lett. Nature 406 (2000) 489.
[19] T. Ito, B.J. Beaudry, K.A. Gschneider Jr., T. Takeshita, Phys. Rev. B 27 (1983) 2830.
[20] K. Kai, K.A. Gschneider Jr., B.J. Beaudry, D.T. Peterson, Phys. Rev. B 40 (1989) 6591.