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Towards a metallic YH_3 phase at high pressure

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Abstract

The switchable mirror compound YH_3 has a high-pressure behavior at variance with current band-structure models. It remains transparent at least up to 25 GPa. At high pressure, the optical gap decreases linearly extrapolating to zero for 55 ± 8 GPa, above which pressure a metallic state is expected. This is in disagreement with a theoretically predicted insulator-to-metal phase transition at 1.5 GPa. In-situ structural studies using synchrotron radiation reveal a 2% drop in the *c*-lattice vector at 4 GPa, while both above and below the phase transition, the spectra are consistent with a hcp structure. Hence this phase transition is probably due to a rearrangement of the hydrogen lattice positions only and the predicted hcp to fcc transition is not observed.

Keywords: Interstitial alloys; Gas solid reaction; Optical materials; High pressure; Synchrotron radiation

1. Introduction

Huiberts et al. [1] discovered that thin films of $YH_{3-\delta}$ can be switched between a reflecting mirror and a transparent insulator by varying their hydrogen content. Already at 1 bar H_2-pressure at room temperature $\delta \simeq 0.2$ is reached and YH_3 is a transparent yellowish insulator. The optical gap is 2.3 eV and the electrical resistivity is higher than 1 Ω cm. YH_3 and related switchable mirror compounds recently attracted a lot of interest not in the least because their electronic structure is still under debate. There are two lines of thought following (i) a band structure, Peierls-like model (e.g. Kelly et al. [2] and Ahuja et al. [3]) and (ii) a strongly correlated electron model (e.g. Ng et al. [4,5] and Eder et al. [6]). Within the band-structure school, two independent first principles calculations [2,3] predict a transition to a metallic YH_3 phase at high pressure. According to the density functional calculation of Kelly et al. [2], a transition from an insulating distorted HoD_3 phase ('Kelly'-phase) to a metallic undistorted HoD_3 phase is expected at 15% decrease of the molar volume, corresponding to 14 GPa applied pressure. However, according to the ab initio calculation of Ahuja et al. [3], the undistorted HoD_3-structure is insulating and stable at ambient pressure, while a phase transition to a metallic cubic phase at 1.5 GPa is predicted. Both predictions are not borne out by the present experiments since we find that YH_3 is still non-metallic well above both predicted phase transition pressures.

In addition to resolving experimentally the phase diagram, the observation of a pressure induced insulator-to-metal (IM) transition would be very valuable, because the IM transition takes place in the undoped (i.e. stoichiometric) semiconductor and hence may be easier to understand from a theoretical point of view than the metal-to-insulator (MI) transition, which takes place in heavily doped semiconducting $YH_{3-\delta}$ with $\delta \simeq 0.2$. We performed several high-pressure experiments using diamond anvil cells (DACs) [7–9] to find evidence both for the structural phase transition and for the IM transition.

In the middle of the culet of one diamond, a film of yttrium is deposited with a thickness of 500 nm and a diameter of 60 μm. The yttrium is protected from oxidation by a 20-nm thick palladium layer [10] covering the whole culet of the diamond. Liquid hydrogen is condensed at its triple point (~14 K) in the gasket of the DAC[1] and serves both to provide the hydrogen for uptake by the

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[1]We use the Teflon seal method as described in Silvera and Wijngaarden [11].

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yttrium film and as a pressure medium. After closure of the DAC, the set-up is warmed up to room temperature, where all experiments described here are performed. Pressure is determined using the ruby fluorescence method and the calibration by Mao et al. [12].

The effect of pressure on the optical properties is rather spectacular. At zero H_2-pressure the as-deposited Y-films have a typical metallic appearance. Transmission is very weak. When brought in contact with H_2-gas at 0.1 MPa, the Y-film readily absorbs H and forms first a metallic cubic dihydride β-$YH_{2-\delta}$ with a weak transparency window at $\hbar\omega \simeq 1.9$ eV and after a few seconds a hcp trihydride γ-$YH_{3-\delta}$ with $\delta \simeq 0.2$. The trihydride is transparent, yellowish and non-metallic [13]. When the H_2-gas pressure is further increased, δ is decreased and at 4 GPa, stoichiometric YH_3 is obtained. This is slightly more transparent than $YH_{3-\delta}$ at 0.1 MPa. A typical stoichiometric YH_3 sample is shown in transmission in Fig. 1a. Above 4 GPa, no further hydrogen is absorbed but the molar volume is steadily reduced and with increasing pressure, the color becomes first orange (Fig. 1b), then red (Fig. 1c) and at still higher pressure there is no transparency left in the visible spectrum: the sample appears black (Fig. 1d) in transmission.

The first transition, due to increasing hydrogen concentration at low pressure, is definitely a MI transition [1,14]; the second transition, where the gap is steadily closing down at high pressure, is a pressure effect only. To further investigate the optical properties, at each pressure a transmission spectrum is measured both through the palladium-covered yttrium film and through an adjacent spot, where only palladium is present. The pure yttrium transmission spectra, obtained by dividing these two spectra, are shown in Fig. 2a (together with fitted curves to be described below) for various pressures.

There are two remarkable features: (i) the width of the transmission edge *narrows* under pressure (the 3.5 GPa curve is already much steeper than the 0 GPa curve) and (ii) the pressure dependence of the edge (see Fig. 2b) has a kink around 6 GPa. The width of the edge is probably due to states in the gap (acceptor and donor states) which are associated with hydrogen vacancies and the narrowing of the transmission edge is evidence for the reduction of the number of these vacancies. Although we have stoichiometric YH_3 for $p > 4$ GPa, the transmission edge is extremely sensitive even to small numbers of impurities.

The quantification of the pressure induced shift in the edge position is complicated by the change of its width.

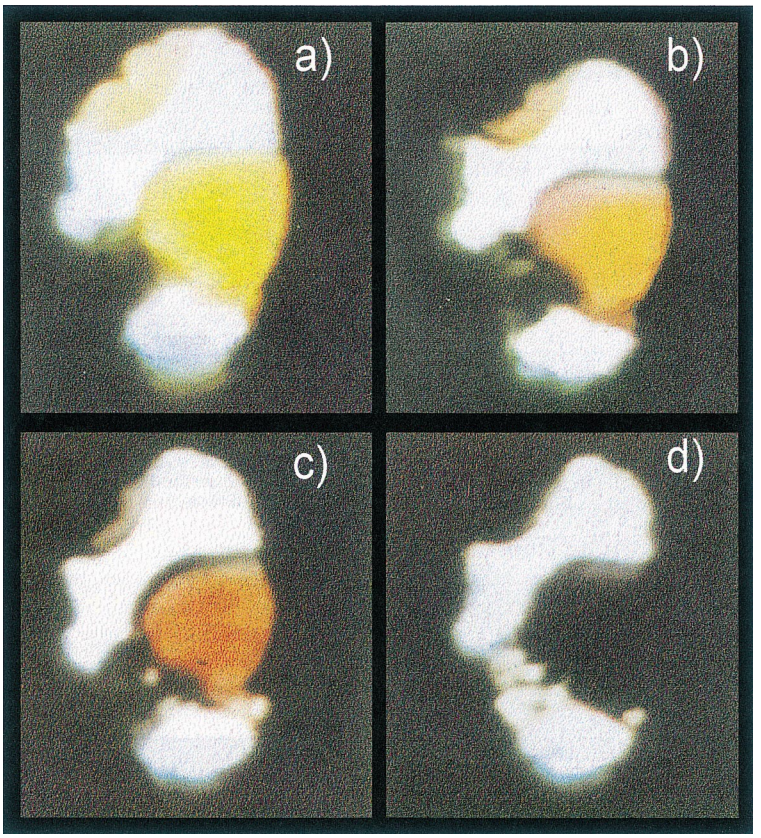

Fig. 1. Transmission photographs of 500-nm thick YH_3 films at high pressure in a diamond anvil cell. There are two samples, one in the centre of the pictures and one at the top left hand corner of the gasket hole which is filled with H_2. At the lower left hand corner of the gasket hole, grains of ruby, used for pressure determination, are visible. Images are taken at 6 GPa (a), 13.6 GPa (b), 20 GPa (c) and 24.8 GPa (d). The sample is yellowish transparent (a) at low pressure, but the transmission shifts towards the red (b and c) to finally disappear completely from the visible spectrum (d).

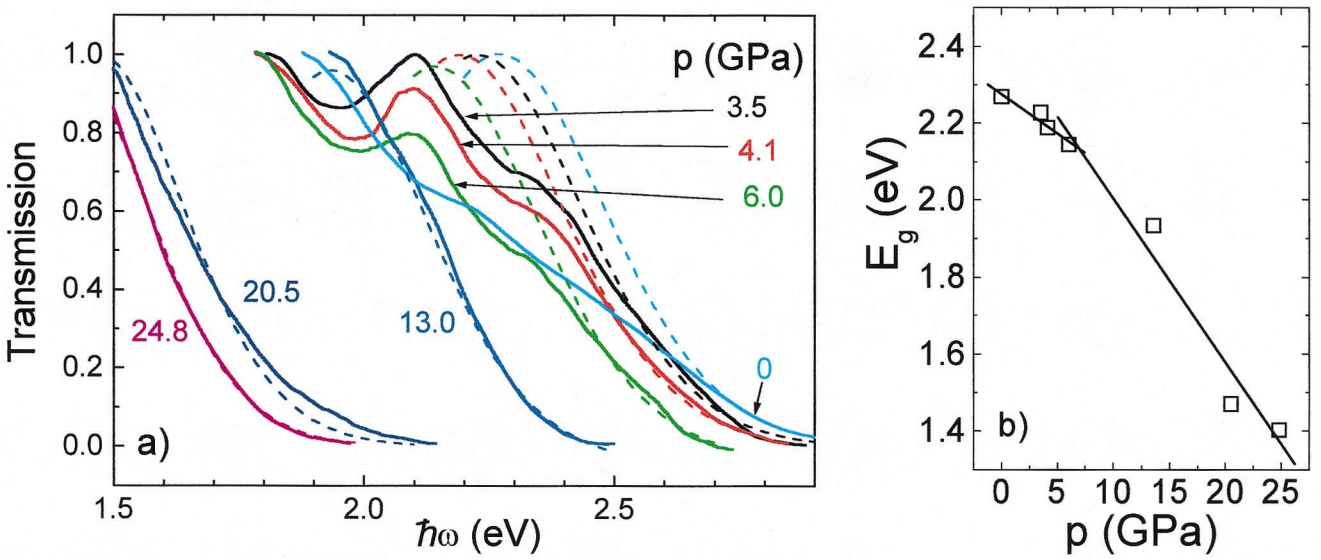

Fig. 2. Experimental transmission spectra (a) of YH_3 under high pressure at various pressures. To determine the pressure dependence of the optical gap E_g, a non-linear fitting procedure[2] is used. The resulting pressure dependence of the optical gap E_g, shown in (b), is -0.020 ± 0.004 eV/GPa below 6 GPa and -0.043 ± 0.006 eV/GPa above 6 GPa. The latter fit extrapolates to a zero gap at 55 ± 8 GPa, where an insulator-to-metal (IM) transition is expected to take place.

Since the broadening is due to subgap states, influencing the low energy part of the edge, a reliable measure for the real gap value can be obtained by fitting the high energy part to a undisturbed gap function. For this we use a non-linear fitting procedure.[2] First such a fit is made to the 24.8 GPa spectrum. The good quality of the fit over the whole measured curve indicates that at this pressure, the role of gap states is negligible. The transmission spectra at lower pressures are fitted with the same slope (i.e. C as defined in footnote 2 is fixed) to further reduce the possible effect of the donor and acceptor states. These fits are shown as dashed curves in Fig. 2a. The corresponding values[3] for the optical gap E_g are shown in Fig. 2b. The pressure dependence of the optical gap is -0.020 ± 0.004 eV/GPa below 6 GPa and -0.043 ± 0.006 eV/GPa above 6 GPa. The high-pressure data extrapolate to a zero gap at 55 ± 8 GPa.

The transmission spectra unequivocally show that YH_3 has a finite optical gap up to at least 24.8 GPa and according to linear extrapolation even up to 55 ± 8 GPa. This is in sharp contrast with the prediction of Ahuja et al. [3] that the high-pressure phase (i.e. above 1.5 GPa) is metallic. Also it is at variance with the prediction of Kelly et al. [2] of a transition to a metallic HoD_3 structure at a volume reduction $\Delta V/V = -15\%$, which corresponds[4] to 14 GPa. This is one of the main conclusions of this paper. We note that the isotope effect [16] in YH_3 and YD_3 is apparently also at variance with the model by Kelly et al [2].

As the occurrence of two slopes in $E_g(p)$, Fig. 2b, may indicate the presence of a structural phase transition, we measured the lattice parameters of YH_3 by X-ray scattering at the ID-09 beamline of the European Synchrotron Radiation Facility in Grenoble. This beamline is ideally suited for diamond anvil cell work because of its high brilliance beam with a diameter of 50 μm. Selected diffraction spectra obtained after subtraction of the diamond background are presented in Fig. 3a. For com-

[2]Experimental transmission data is fitted to the equation:

$$T(\hbar\omega)=\exp\left\{-C\frac{(\hbar\omega+E_g)^2}{\hbar\omega}\right\},$$

T is the transmission as a function of photon frequency ω, while C and E_g are fitting constants. E_g determines the position and C the slope. The equation is based on the formula $\alpha\sim(\hbar\omega+E_g)^r/\hbar\omega$ for the absorption coefficient α due to excitation of electrons to extended states in a semiconductor. We use $r=2$. See Wood and Tauc [15].

[3]The gap values E_g used here are defined by the fitting procedure described in footnote 2; they correspond to the maximum of the fitted transmission edge. The value of 1.8 eV, which is often quoted from Ref. [1], corresponds to the same part of the measured transmission edge. Due to the extreme broadening of the ambient pressure curve these values are quite different at $p=0$. Note, however, that in Ref. [1] the transmission edge also extends to 2.8 eV.

[4]To convert the 15% volume reduction to the phase transition pressure p_c, we first take the volume jump of 2% at ~4 GPa into account (see Fig. 4). To calculate the pressure p_c for the remaining 13% compression, the bulk modulus is needed, which is unfortunately not known experimentally for YH_3. From our X-ray experiments (Fig. 4) a crude upper bound estimate $B=163\pm25$ GPa can be made. From first principles band structure calculations, P. Van Gelderen (private communication) finds $B=110$ GPa for the cubic phase. Sun et al. [17] find $B=99$ GPa for the cubic phase, while from the total energy curves of Ahuja et al. [3] we find that $B=99$ GPa for the HoD_3 phase and $B=128$ GPa for the high-pressure fcc phase. Taking $B=110$ GPa as a reasonable estimate, we find $p_c=14$ GPa.

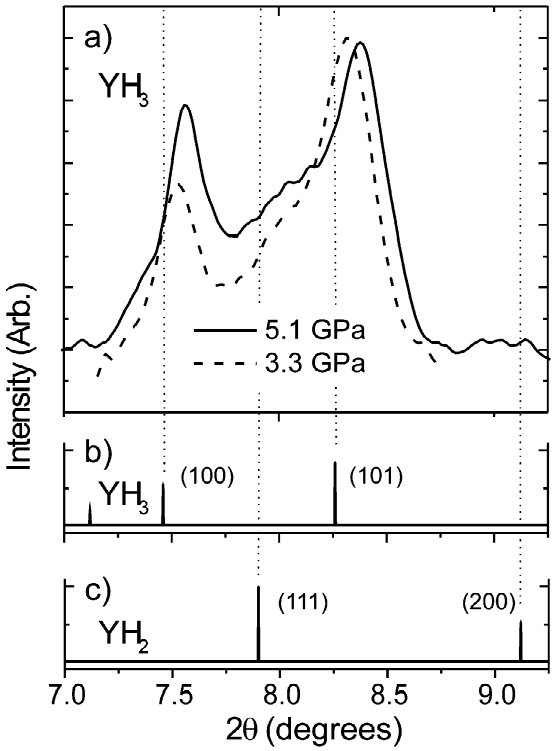

Fig. 3. (a) X-ray diffraction spectra obtained at the ESRF Synchrotron facility with 0.41345 Å radiation, above and below the high-pressure structural phase transition of YH_3. For comparison zero-pressure spectra for hcp YH_3 (b) and for fcc YH_2 (c) are also indicated. Clearly, both high-pressure spectra shown in (a) are consistent with a hexagonal phase as in (b) but not with a cubic phase as in (c).

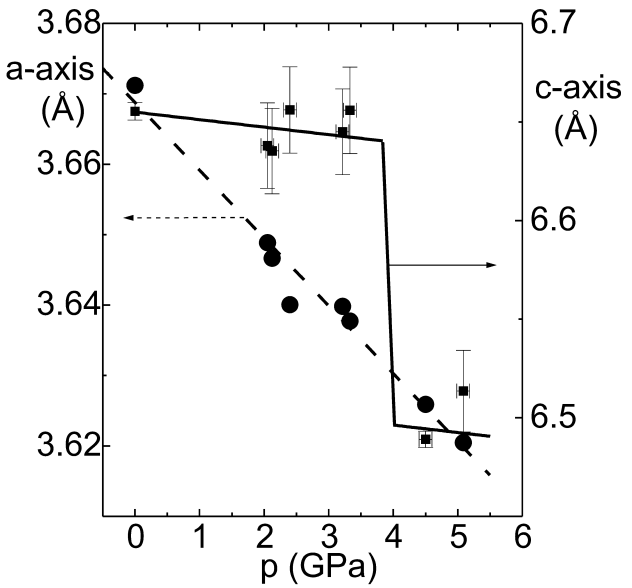

Fig. 4. Pressure dependence of the *a*- and *c*-lattice parameters of YH_3. A rearrangement of hydrogen atoms is probably responsible for the jump in *c* around 4 GPa.

parison, also the peak positions of the zero-pressure hcp YH_3 phase are shown in Fig. 3b and of the zero-pressure fcc YH_2 phase in Fig. 3c. Although the high-pressure spectra are broader, it is clear (i) that both high-pressure spectra are similar to the hcp zero-pressure YH_3 phase, although the peaks are shifted to higher angles (corresponding to smaller lattice spacing due to the compression) and (ii) that between 3.3 and 4.4 GPa there is a rather abrupt change in position, which could be indicative of a phase transition.

For three reasons, the most likely candidate for the high-pressure phase would be the fcc phase: (i) such a transition was predicted by Ahuja et al. [3], (ii) it is known that the energy difference between the hcp and fcc phases is usually very small and (iii) YH_2 is fcc as are several rare-earth trihydrides (but not YH_3) at zero pressure. We find, however, that the spectrum measured at 4.4 GPa is inconsistent with a fcc structure. This is immediately evident from the comparison with the fcc YH_2 spectrum, shown in Fig. 3c. Hence it is likely that the crystal structure remains hcp and that the phase transition at 4 GPa involves only a rearrangement of the hydrogen positions due to a change from the 'Kelly'-structure [2] to the HoD_3 structure. The pressure dependence of the hcp *a*- and *c*-lattice vectors obtained from the X-ray spectra is shown in Fig. 4. The pronounced drop in the *c*-axis lattice vector around 4 GPa shows that there is indeed a first-order structural phase transition.

In conclusion, a pressure induced phase transition is observed at 4 GPa, much higher than theoretically predicted by Ahuja et al. [3] and much lower than predicted by Kelly et al. [2]. The high-pressure structural data is consistent with the hcp structure and the phase transition is probably due to a rearrangement of the hydrogen positions. The very existence of this high-pressure hcp structure is at variance with the theoretical prediction of Ahuja et al. [3]. Optical transmission spectra show that the semiconductor gap remains open until at least 25 GPa. Extrapolating the pressure dependence of the gap, an insulator to metal transition is expected at 55 ± 8 GPa. These pressures are much higher than theoretically predicted [2,3] but are in the range accessible by DAC experiments. Metallic YH_3 is expected to have interesting physical properties (e.g. superconductivity) as the H-derived electronic bands at the Fermi energy are strongly coupled to the optical phonons.

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