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Short Communication

Pressure tuning of optical reflectivity in LuH_2

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In the last few years, interest in the rare-earth hydrides has been reinvigorated owing to their potentials for hosting room-temperature superconductivity under achievable pressures. Prominent examples include LaH_{10} and YH_9, in which the superconducting transition temperature (T_c) approaches 260 K at ~200 GPa [1–4]. Nitrogen (N) doped lutetium hydride was recently claimed to exhibit possible superconductivity at a room temperature of 294 K under near-ambient pressure of ~1 GPa, concomitant with remarkable color changes from lustrous blue to pink and subsequently bright red with increasing pressures (a few GPa) [5]. Similar color changes have been observed shortly by a few independent studies on both N-free and N-doped LuH_2, but no superconductivity was observed up to ~50 GPa [6–9]. The peculiar color changes motivate us for further investigation using optical spectroscopy. Here we report the optical reflectivity measured for LuH_2 from visible to near-infrared region (420–900 nm) at different pressures up to ~14 GPa. We observe strong absorption of red light close to a sharp plasma edge near 750 nm at ambient conditions. Such plasma edge blueshifts with a pressure coefficient of 9.4–12.6 meV/GPa, resulting in the increase of red-light reflection and blue-light absorption. Our work thus unveils the dominant role of pressure modulated plasma frequency ω_p for the color changes observed in LuH_2.

We start with the commercially purchased LuH_2 powder (99.9%) from JiangXi Viilaa Metal Material Co., Ltd. Rietveld refinements on the powder X-ray diffraction (XRD) pattern (Fig. S1 online) confirmed that the major phase is the cubic LuH_2 with the fluorite structure (space group $Fm\bar{3}m$), coexisting with a minor phase of Lu metal and unidentified phases marked with asterisks. The blue shining grains of LuH_2 were pre-compressed to flat platelets (measuring 5–10 μm in thickness) using tungsten carbide anvils. These platelets were loaded into the symmetric diamond anvil cells (DACs) with 300 μm culets and T301 stainless steel gaskets, in the middle of which ~180 μm diameter hole was drilled and served as the sample chamber. Soft and transparent KBr was employed as the pressure transmitting medium. Silver is known to possess near-unity reflectivity in the visible to near-infrared spectral range and thus was mounted inside the DAC as the reflection reference. The pressure inside DAC was determined from the shift of ruby fluorescence lines. For the optical reflectivity measurements [10,11], broadband radiation from a supercontinuum laser (NKT FIU-6) was guided and focused into the DAC with a 10× objective. The reflected beam was collected by the same objective and detected by a spectrometer coupled with a CCD camera (Princeton Instrument). The reflectivity of LuH_2 is obtained by calculating the ratio between the reflection intensity from LuH_2 and that from the silver mirror. Sample observations and snapshots are conducted without alternating the measurement system (see more details in Fig. S2 online).

Displayed in Fig. 1 are the micrographs of LuH_2 sample 1 at different pressures. The sample exhibits a shiny blue color at ambient conditions and immediately turns into violet after direct contacting with the diamond culet. The color of the sample changes to dark red around ~3 GPa and then orange at pressures above ~12 GPa. These new results are supplementary to our previous work [6] and confirmed pressure-induced continuous color changes in LuH_2. The corresponding reflectivity spectra are shown in Fig. 2a. At ambient conditions, the reflectivity is relatively large at longer wavelengths above ~750 nm, indicating efficient screening of electric fields of the light by the charge carriers in LuH_2 and supporting its conductive nature in the DC limit [12,13]. Meanwhile, there is a sharp suppression of the red reflection (<~0.03) near 675 nm and the reflectivity goes up at shorter wavelengths. These are typical features of a plasmon resonance, near which the collective excitation of electrons causes sign change of the real part of the dielectric function. The reflectivity hence has a pro-

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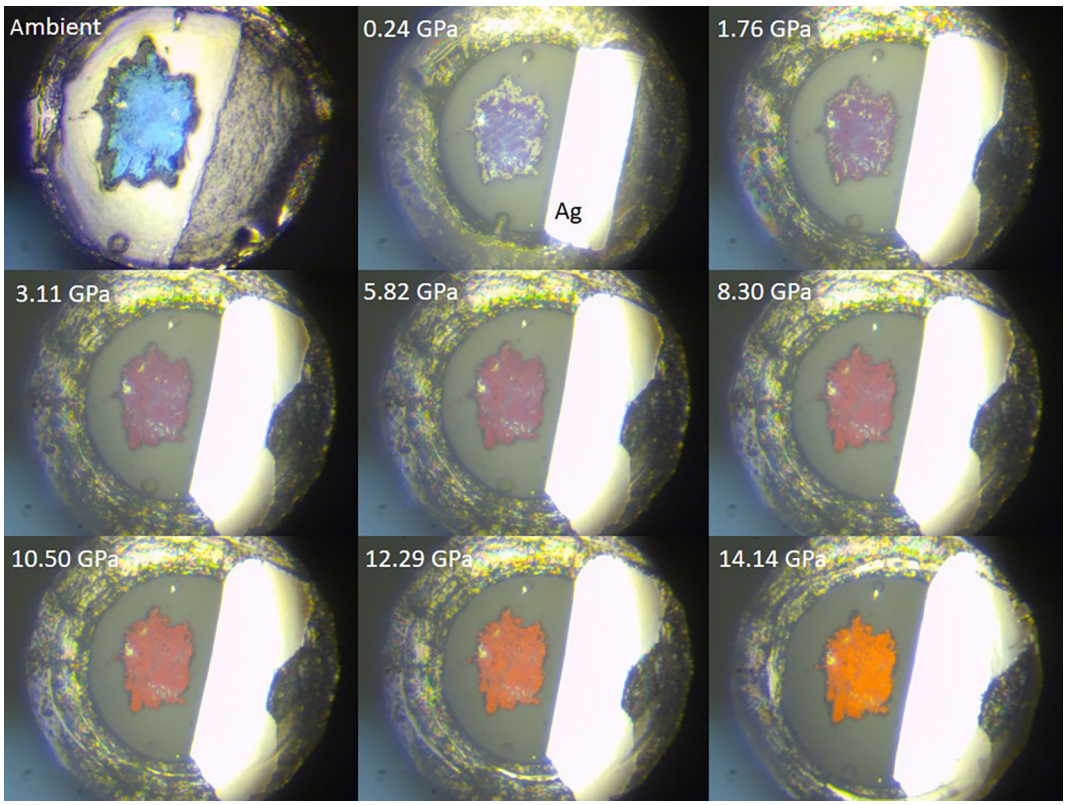

Fig. 1. (Color online) Optical micrographs of the LuH_2 sample 1 at different pressures. A small piece of silver near the sample is used as the reflection reference. The color of the sample changes from shiny blue at ambient pressure to dark red around ~3 GPa, then becomes bright orange at higher pressures (>~12 GPa).

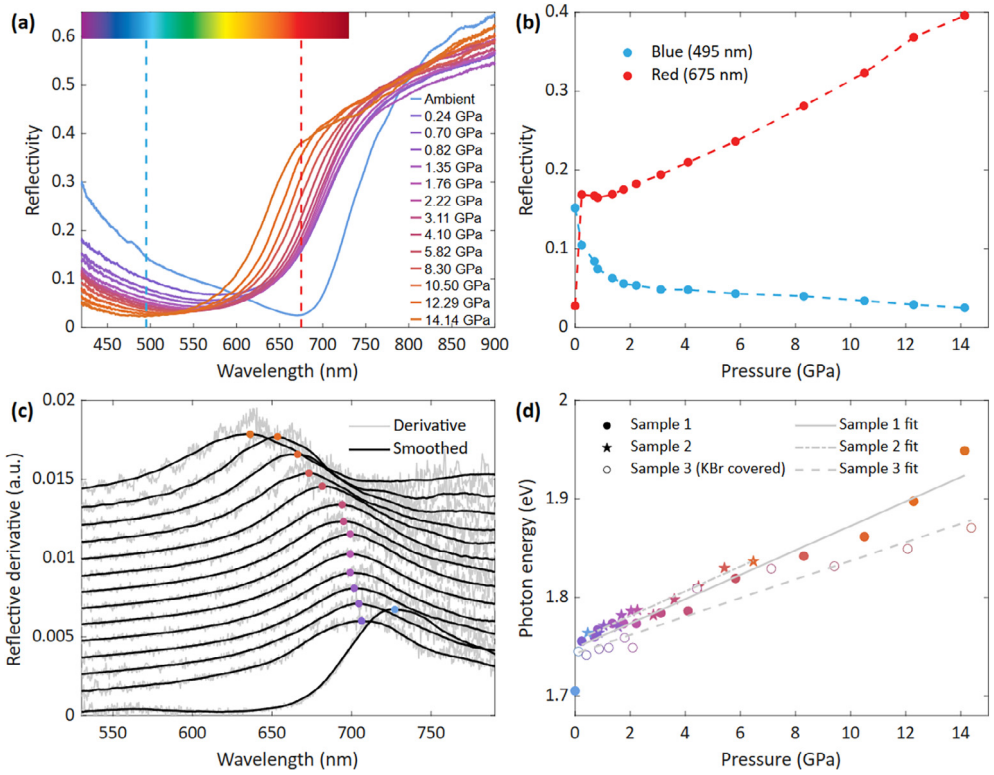

Fig. 2. (Color online) (a) Optical reflectivity spectra of LuH_2 (sample 1) measured with varying pressures. The sharp change in reflectivity corresponds to the LuH_2 plasma edge, which blueshifts when the pressure goes up, resulting in the increased reflection of red light and suppressed reflection of blue light. The process is consistent with the color change observed in Fig. 1. (b) The evolution of reflectivity with pressure at two selective colors (495 nm blue and 675 nm red, respectively). (c) The plasmon resonance estimated from the peak of reflectivity derivative. (d) The plasma energies as functions of pressure for samples 1–3 and the corresponding linear fits.

nounced minimum near the sharp plasma edge. It also explains the initial bluish color seen in Fig. 1. The results are consistent with the literature and suggest high quality of our LuH_2 samples [14].

With increasing pressure, the plasma edge continuously shifts to higher energies. The reflection of blue and red at representative wavelengths (495 and 675 nm, respectively, highlighted by the dashed vertical lines in Fig. 2a) are extracted and shown in Fig. 2b. The boost of red reflection and the continuous suppression of the blue reflection confirm the color change observed through the optical microscope (Fig. 1). In Fig. 2c, we estimate the plasma energy $\hbar\omega_p$ (or the plasma edge) by finding the peak in the reflectivity derivatives. The extracted peak energy as a function of pressure is plotted in Fig. 2d for three different samples. The upper surface of the sample 1 and 2 under pressure is in direct contact with the DAC, while for sample 3, the upper surface is in contact with KBr. As can be seen, all the three samples feature similar positive pressure coefficients, i.e., (12.4 ± 0.7), (12.6 ± 0.8), and (9.4 ± 0.8) meV/GPa, respectively. We noticed discontinuity of the reflectivity (Fig. 2b) and plasma energy (Fig. 2d) upon increasing pressure from ambient for sample 1 (similarly for sample 2). It is likely due to the fact that the sample experiences a considerable stress that cannot be accurately measured by the ruby calibration during the initial compression on the sample directly with DAC. By contrast, the surface of sample 3 touches the soft KBr and should experience less stress during the initial compression. However, the strong cavity interference severely hinders the accurate measurement of the reflectivity spectrum and causes larger uncertainty of the extracted pressure coefficient (see more details in Fig. S4 online).

The electronic band structures of LuH_2 at ambient and under pressures have recently been calculated [12,13]. Our experimental observations are in general agreement with those calculations. For example, the LuH_2 is a metallic phase and thermodynamically stable at near-ambient pressures, and the interband transition in LuH_2 has positive pressure coefficients. However, without considering the intraband transitions and plasmon modes, the calculated absorption spectra in Ref. [12] do not match the experiments in the long wavelengths. Meanwhile, there is likely absent of any structural phase transitions in the applied pressure range, consistent with the theoretical calculation that LuH_2 is thermodynamically stable below ~5 GPa [13]. The pressure induced shift of plasma energy $\hbar\omega_p$ is possibly due to the downward movement of the conduction bands with increasing pressures as shown in Ref. [13]. Such process enhances the conduction band occupancy and hence the plasma frequency blueshifts as $\omega_p \propto n^{1/2}$, where n is the electron concentration.

To summarize, the reflectivity of LuH_2 changes significantly in the visible range due the plasmon resonance, which continuously shifts to higher energies with increasing pressure. Our work sheds light on resolving the puzzles regarding the pressure modulated color changes in both N-free and N-doped lutetium hydrides [5–9].

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

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Author contributions

Jinguang Cheng and Yang Xu designed and supervised the whole research. Pengfei Shan and Ningning Wang prepared the samples and set the pressure environments. Xuan Zhao performed the optical experiments. Yunliang Li did some preliminary optical measurements. Xuan Zhao, Pengfei Shan, Yang Xu, and Jinguang Cheng wrote the manuscript with input from all authors. All authors discussed the experimental details and results.

Appendix A. Supplementary materials

Supplementary materials to this short communication can be found online at https://doi.org/10.1016/j.scib.2023.04.009.

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