

Pressure-Induced Color Change in the Lutetium Dihydride LuH₂

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The lutetium dihydride LuH₂ is stable at ambient conditions. Here we show that its color undergoes sequential changes from dark blue at ambient pressure to pink at ~ 2.2 GPa and then to bright red at ~ 4 GPa upon compression in a diamond anvil cell. Such a pressure-induced color change in LuH₂ is reversible and it is very similar to that recently reported in the N-doped lutetium hydride [*Nature* **615**, 244 (2023)]. However, our preliminary resistance measurements on LuH₂ under pressures up to ~ 7 GPa evidenced no superconductivity down to 1.5 K.

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The recent discovery of high-temperature superconductivity in LaH₁₀^[1,2] with the clathrate structure has reignited great enthusiasm on the explorations of rare-earth hydrides with an aim to achieve room-temperature superconductivity. Among the 14 rare-earth elements, lutetium (Lu) is the heaviest one and has the smallest metallic radius, and it may be the least naturally abundant. Theoretical studies on the Lu–H system have predicted high-temperature superconductivity at relatively low pressures, e.g., the *Im* $\bar{3}m$ LuH₆ with $T_c \approx 273$ K at 100 GPa.^[3] Experimentally, several Lu hydrides have been reported so far. The Lu dihydride LuH₂ with the fluorite structure is stable at ambient conditions,^[4] and it shows a metallic conductivity.^[5,6] By heating a Lu foil with ammonia borane (NH₃BH₃) in a diamond anvil cell (DAC) at about 110 GPa, Shao *et al.* have obtained a superconducting LuH₃ with the critical temperatures in the range of $T_c = 12\text{--}15$ K over the pressure range 110–170 GPa.^[7] When the synthesis pressure of the above reaction in DAC is elevated to 184 GPa, Li *et al.* reported the formation of a new polyhydride with the possible formula of Lu₄H₂₃, which adopts a higher H content and shows higher T_c reaching 65–71 K over the pressure range 180–218 GPa.^[8] Surprisingly, Dias and coworkers recently reported that N-doped Lu hydride exhibits room-temperature superconductivity at a remarkably low pressure of 1 GPa.^[9] According to this report, the sample was recovered from the reaction of a thin Lu foil with H₂/N₂ (99:1) mixture in DAC at 2 GPa and 65 °C for overnight. It shows a shining blue color at ambient pressure. Intriguingly, the sample's color was observed to change from blue to pink in the pres-

sure range 0.3–3 GPa (phase II) and then to red at pressures above 3 GPa (phase III). Moreover, the pink-colored phase II was found to exhibit room-temperature superconductivity with the maximum $T_c = 294$ K achieved at about 1 GPa. Based on the XRD results, the authors have attributed the superconducting phase II to the major phase of LuH_{3- δ} N _{ϵ} (92.25%) coexisting with the minor phases of LuN_{1- δ} H _{ϵ} (7.29%) and Lu₂O₃ (0.46%).^[9] This discovery has immediately aroused worldwide interest and will no doubt stimulate extensive studies on the Lu hydrides. Here, we focus on the ambient-stable dihydride LuH₂ and report on the observation of pressure-induced color change upon compression in a fashion similar to that in the N-doped Lu hydride.^[9] Unfortunately, we did not observe superconductivity in LuH₂ down to 1.5 K under pressures up to 7.7 GPa.

Results. We purchased the “Lu” powder (L110933-1 g, 99.9% metal basis) from Aladdin. As shown in the inset of Fig. 1, the as-received powder is dark blue in color, whereas the Lu in the pure form is expected to be silvery white. Such a difference motivated us to verify its phase purity by measuring the powder XRD at room temperature. It turns out that the as-received “Lu” powder actually is a mixture of LuH₂ and Lu₂O₃ with only a small portion of Lu. Two additional weak peaks at 37.51° and 54.06° marked by asterisks in Fig. 1 come from some unknown phases, which thus cannot be considered in the Rietveld refinement. Based on the scaling factors of the Rietveld refinement on the XRD pattern in Fig. 1, their percentages are estimated to be 69.6(3)%, 27.1(6)%, and 3.3(1)% for LuH₂, Lu₂O₃, and Lu, respectively. The lattice parameter

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of LuH_2 is calculated to be $a = 5.02949(8) \text{ \AA}$, which agrees well with the reported value of 5.033 \AA in the literature.^[4] We noted that the obtained lattice parameter of LuH_2 is very close to that of $a = 5.0289(4) \text{ \AA}$ for the main phase of N-doped Lu hydride, i.e., compound A mentioned in Ref. [9]. Because the Lu_2O_3 powder is white in color, the dark blue color of the as-received Lu powder should be attributed to the major phase LuH_2 .

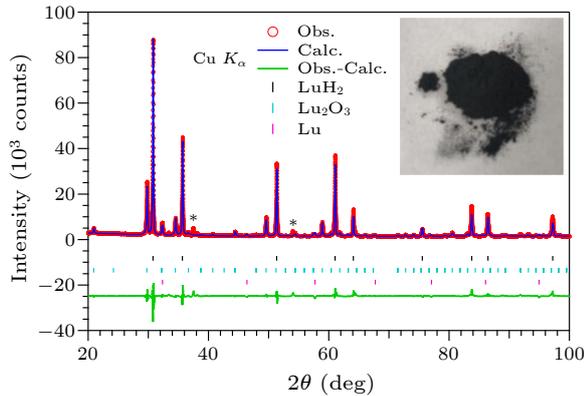


Fig. 1. Rietveld refinement on the XRD pattern of the as-received “Lu” powder from Aladdin. Inset: the photograph of the “Lu” powder.

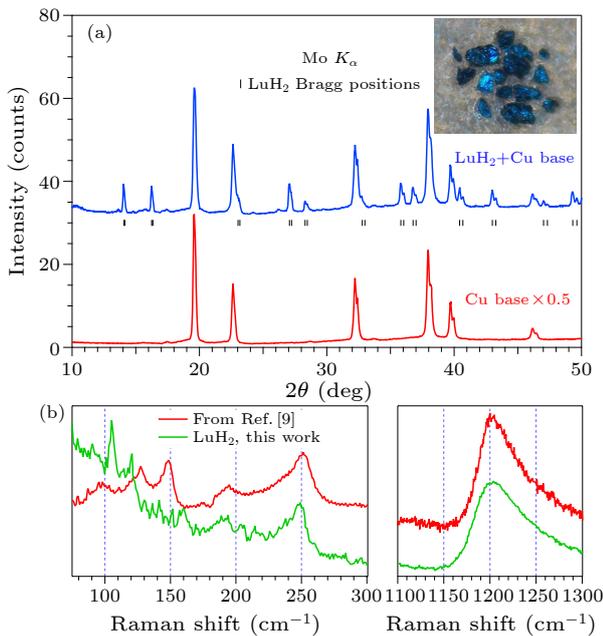


Fig. 2. (a) The XRD patterns of the LuH_2 grains together with the Cu base (top) and the Cu base only (bottom). Inset: the photograph of the LuH_2 grains. (b) The Raman spectra of the LuH_2 grain collected at ambient condition together with that of N-doped Lu hydride (Extended data Fig. 1 in Ref. [9]) for comparison.

About 100 mg of the above-mentioned $\text{LuH}_2 + \text{Lu}_2\text{O}_3 + \text{Lu}$ mixture powder and 200 mg of CaH_2 contained in separated Al_2O_3 crucibles are sealed together in a quartz tube and then heated at $200 \text{ }^\circ\text{C}$ for five hours. We found that such a treatment did not change the relative ratio

of the components in the mixture. However, a closer inspection of the powder under microscope reveals the presence of some shining grains in the blue color and with dimensions about $40\text{--}50 \mu\text{m}$, as seen in the inset of Fig. 2(a). Interestingly, the color of these grains is very similar to that of N-doped Lu hydride reported by Dias and coworkers.^[9] We then selected several grains and conducted XRD measurements by using a custom-designed instrument equipped with a Xenocs Genix3D Mo K_α (17.48 keV) x-ray source. This source produces a beam spot size of $150 \mu\text{m}$ at the sample position and provides 2.5×10^7 photons/s. These grains shown in the inset of Fig. 2(a) were attached to a copper (Cu) base and then mounted on a Huber 4-circle diffractometer. Diffraction signals are collected by a highly sensitive single-photon counting PILATUS3 R 1M solid state area detector with 981×1043 pixels. Each pixel size is $172 \mu\text{m} \times 172 \mu\text{m}$. The XRD pattern was measured in the reflection geometry, with the incident angle rotating from 1° to 31° .

The top XRD pattern in Fig. 2(a) contains the signals from both the samples and the Cu base, while the bottom profile displays only the diffraction from the Cu base. The observed double peaks arise from the Mo K_{α_1} ($\lambda = 0.7903 \text{ \AA}$) and K_{α_2} ($\lambda = 0.7136 \text{ \AA}$) lines. Excluding the diffraction peaks from the Cu base, the remaining peaks match well with the calculated ones of LuH_2 with the cubic $Fm\bar{3}m$ space group and lattice parameter $a = 5.02949 \text{ \AA}$. In the LuH_2 structure, the Lu atom is bonded in a body-centered cubic geometry to eight equivalent H atoms with the Lu–H bond lengths being 2.1778 \AA . For comparison, we prepared the Lu trihydride LuH_3 by treating the “Lu” and NH_3BH_3 at 4 GPa and $1000 \text{ }^\circ\text{C}$ for 30 min in a large-volume Kawai-type multianvil module. From the XRD measurement at ambient conditions, the calculated lattice parameter $a = 5.16295(3) \text{ \AA}$ of LuH_3 is much larger than that of LuH_2 . By using the above process, we thus successfully isolated LuH_2 grains with blue color.

To further characterize these LuH_2 grains, we also collected the Raman spectra at ambient condition by using a confocal Raman system (MonoVista CRS + 500, Spectroscopy & Imaging GmbH) with 532 nm laser excitation. The obtained spectra are displayed in Fig. 2(b) and compared with those of N-doped Lu hydride given in Ref. [9] (Extended data Fig. 1). For LuH_2 , we observed pronounced Raman peaks at 250 and 1200 cm^{-1} , which are identical to those of N-doped Lu hydride.^[9] However, some obvious differences are observed in the Raman spectra below 160 cm^{-1} .

After obtaining and isolating these blue grains of LuH_2 , we loaded one piece of grain into the DAC of $300 \mu\text{m}$ culet and monitored its color change upon compression at room temperature. The pressure inside DAC was determined from the shift of Ruby fluorescence lines at room temperature, and the soft KBr was employed as the pressure transmitting medium. Figure 3 shows the obtained microphotographs of LuH_2 at different pressures. As can be seen, the blue color of LuH_2 first changes to pink at 2.23 GPa ,

and then to bright red at pressures above ~ 4 GPa. After releasing pressure from 5.7 GPa to 0 GPa, its color returns to the original dark blue, confirming that the color change upon compression is reversible. These observations are stunningly similar to those of N-doped Lu hydride reported by Dias and coworkers,^[9] even though the critical pressures for the color changes are slightly different. Such a difference may arise from the distinct sample forms in these two studies, e.g., the fine powder in Ref. [9] versus the dense grain in the present study. Nonetheless, our present results demonstrate unambiguously that LuH₂ undergoes pressure-induced color change in a moderate pressure range. The origin of such a phenomenon deserves further investigations.

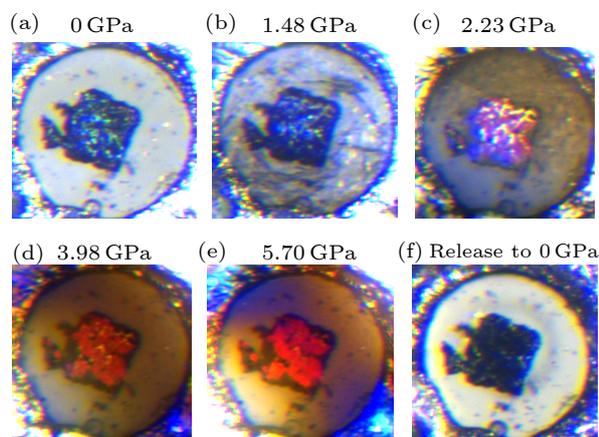


Fig. 3. The microphotographs of the LuH₂ grain with a size of approximately $40\ \mu\text{m} \times 40\ \mu\text{m}$ in the DAC chamber at different pressures: (a) 0 GPa, (b) 1.48 GPa, (c) 2.23 GPa, (d) 3.98 GPa, (e) 5.70 GPa, and (f) 0 GPa after decompression.

LuH₂ shows the metallic behavior at ambient pressure.^[5,6] To check how the transport properties of LuH₂ evolve with pressure accompanying the color change, we further measured its temperature-dependent resistance under different pressures by employing the four-probe method in DAC with $300\ \mu\text{m}$ culet. A piece of LuH₂ grain was loaded into the gasket hole filled with soft KBr as pressure transmitting medium, and four Pt electrodes were put into contact directly with the sample. The pressure was calibrated at room temperature by using the ruby fluorescent method as performed above. The temperature-dependent experiments from 300 to 1.5 K were carried out in a liquid-helium cryostat equipped with a resistance heater on the sample mount for the warming-up control.

Figure 4 shows the obtained resistance $R(T)$ curves at three pressures. The inset photographs further confirm the color changes upon compression. For each measurement, we have given in Fig. 4 the pressure values at room temperature before cooling down and after warming up the DAC. As can be seen, the pressure always increases after one thermal cycle. In addition, the pressure value in DAC may also experiences significant changes upon varying temperatures due to the thermal contraction/expansion of the DAC body. These factors render some strange up-down

features, relatively low data quality, and irreversibility of cooling-down/warming-up $R(T)$ curves, especially at the lower pressures and in the high-temperature region. For these reasons, we will not consider the detailed features of these $R(T)$ curves but extract only the immediate messages from our results: (1) LuH₂ remains in the metallic state with a relatively low resistance, and (2) superconductivity was not observed down to 1.5 K in the studied pressure range. In addition, it is noted that the absolute value of resistance first decreases from 0.7 to 3 GPa and then increases from 3.7 to 6.7 GPa. A weak upturn in $R(T)$ appears in the low temperature region at 6.7(7.7) GPa. Measurements of $R(T)$ under better hydrostatic pressure conditions are needed in the future in order to obtain reliable information about the pressure effect on the transport properties of LuH₂.

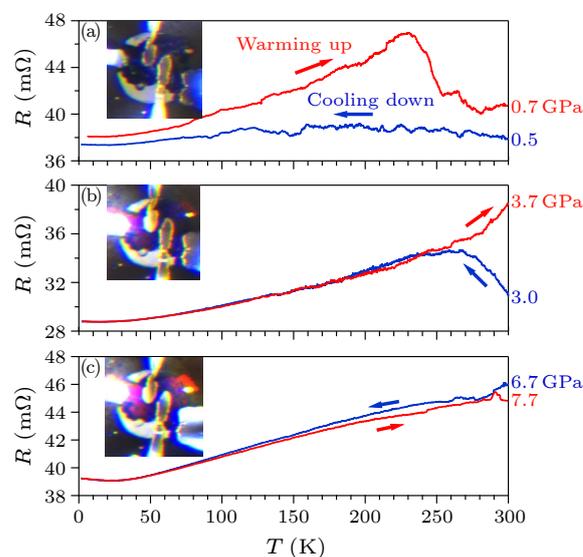


Fig. 4. Temperature dependence of resistance $R(T)$ of the LuH₂ sample at three pressures: (a) 0.5(0.7) GPa, (b) 3.0(3.7) GPa, and (c) 6.7(7.7) GPa. The inset photographs clearly illustrate the color changes of the sample upon compression.

In summary, we have successfully isolated large grains of Lu dihydride LuH₂ and demonstrated that its color changes consecutively from blue at ambient pressure to pink at 2.23 GPa and then to bright red at ~ 4 GPa. Such a pressure-induced color change in LuH₂ is reversible and it is very similar to that observed by Dias and coworkers in the N-doped Lu hydride. Unfortunately, our preliminary resistance measurements on the LuH₂ sample under pressures up to 7.7 GPa reveal the absence of superconductivity down to 1.5 K.

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