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No evidence of superconductivity in a compressed sample prepared from lutetium foil and H_2/N_2 gas mixture

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ABSTRACT

A material described as lutetium–hydrogen–nitrogen (Lu-H-N in short) was recently claimed to have "near-ambient superconductivity" [Dasenbrock-Gammon *et al.*, Nature **615**, 244–250 (2023)]. If this result could be reproduced by other teams, it would be a major scientific breakthrough. Here, we report our results of transport and structure measurements on a material prepared using the same method as reported by Dasenbrock-Gammon *et al.* Our x-ray diffraction measurements indicate that the obtained sample contains three substances: the face-centered-cubic (FCC)-1 phase (*Fm*-3*m*) with lattice parameter a = 5.03 Å, the FCC-2 phase (*Fm*-3*m*) with a lattice parameter a = 4.755 Å, and Lu metal. The two FCC phases are identical to the those reported in the so-called near-ambient superconductor. However, we find from our resistance measurements in the temperature range from 300 K down to 4 K and the pressure range 0.9–3.4 GPa and our magnetic susceptibility measurements in the pressure range 0.8–3.3 GPa and the temperature range down to 100 K that the samples show no evidence of superconductivity. We also use a laser heating technique to heat a sample to 1800 °C and find no superconductivity in the produced dark blue material below 6.5 GPa. In addition, both samples remain dark blue in color in the pressure range investigated.

Room-temperature superconductors have been sought by physicists for more than a century and are considered as a holy grail of the condensed matter physics field. Since such materials conduct electrons with zero resistance and expel magnetism at room temperature, they are expected to revolutionize everyday life. Recently, Dasenbrock-Gammon *et al.*[1] reported evidence of near-ambient superconductivity in a pink material called lutetium–hydrogen–nitrogen (Lu-H-N), which has attracted worldwide attention.[2–16] However, this report has also sparked an intense debate, because some related experiments performed recently[8,12] show that no superconductivity is observed in samples synthesized by alternative methods, such as through the use of a mixture of NH_4Cl and CaH_2 as hydrogen and nitrogen sources at high pressure and high temperature,[8,12] or through the use of ammonia borane as the hydrogen and nitrogen source at low pressure with a laser heating technique.[3] In addition, the color change from blue to pink, considered a unique characteristic of this room-temperature superconductor, has not been observed in these investigations, especially in the pressure range reported by Dasenbrock-Gammon *et al.*[1] In the present study, we prepared a sample following the same procedure as described in Ref. 1 and conducted high-pressure resistance and magnetic susceptibility measurements on it, with the aim of clarifying the ongoing debate.

A lutetium foil (99.9%) with dimensions of 110 × 110 × 40 μm^3 was placed into the gasketed hole in a diamond anvil cell (DAC), which was then placed in a glovebox with an argon atmosphere to exclude air and moisture. The DAC was compressed to ~2.3 GPa, after which it was removed from the glovebox and placed into a gas loading system. Prior to gas loading, the system had been flushed three times with a mixed gas of compressed hydrogen (99%) and nitrogen (1%) to dilute the oxygen content in the chamber. The DAC with the preloaded lutetium foil was opened in the gas loading

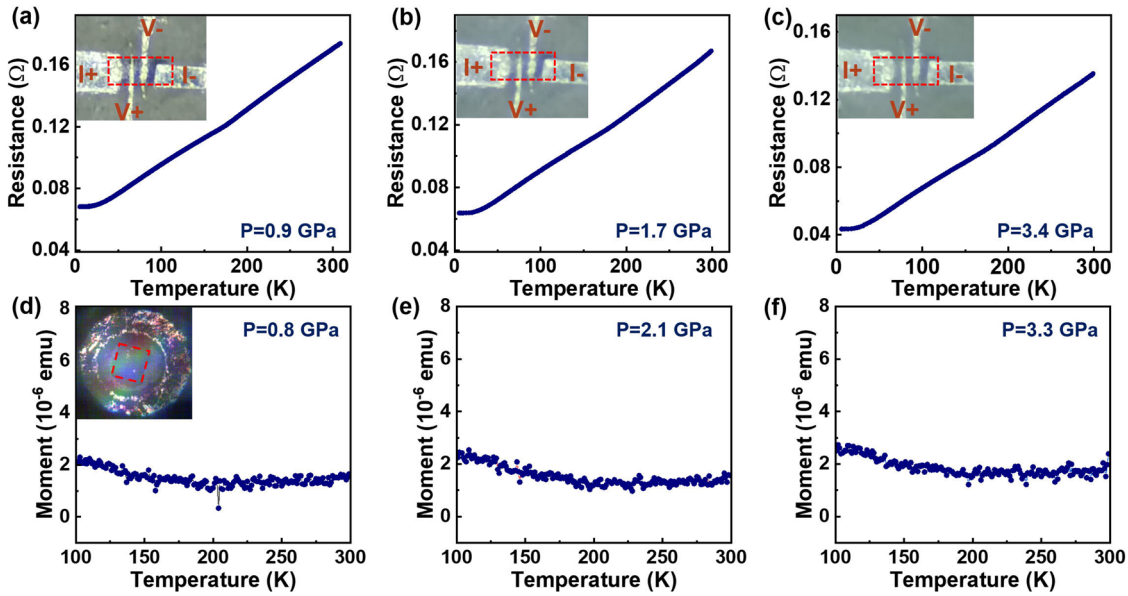

FIG. 1. Transport measurements for the sample obtained at 65 °C at low temperature and high pressure. (a)–(c) Temperature dependence of resistance measured in the pressure range 0.9–3.4 GPa. The insets show the arrangements of the sample and the standard four probes; the sample is indicated by the red dashed box. (d)–(f) Magnetic susceptibility vs temperature measured in the pressure range 0.8–3.3 GPa and temperature range 100–300 K. The data were obtained with background subtraction. The inset in (d) shows the sample in a gasket hole. Our resistance and magnetic results demonstrate that there is no evidence of superconductivity in the sample.

system to allow the gas mixture to enter the sample hole. It was then closed again while still in the gas loading system and pressurized to 2.0 GPa with a remote gear controlling device. The DAC was then heated to 65 °C in a furnace and kept at this temperature for 24 h. The obtained sample appeared dark blue in color under transmitted white light [see the inset in Fig. 1(a)], which is consistent with what was reported by Dasenbrock-Gammon *et al.*[1]

Next, we performed high-pressure resistance measurements on the sample using the standard four-probe method. Figures 1(a)–1(c) show the temperature dependence of the resistance in a pressure range covering that reported by Dasenbrock-Gammon *et al.*[1] It was found that the resistance decreased upon cooling and exhibited a saturation behavior at lower temperatures, which is typical metallic behavior. When the pressure was increased to 3.4 GPa, the resistance exhibited the same trend vs temperature. No drop in resistance was observed down to 4 K, indicating that this sample (henceforth referred to as "the sample obtained at 65 °C") was not superconducting under these conditions. To determine its magnetic properties, we conducted high-pressure magnetic susceptibility measurements in a similar pressure range. As can be seen in Figs. 1(d)–1(f), the temperature dependence of the magnetization displayed no diamagnetic signal, further confirming the absence of superconductivity in the studied sample.

We carried out x-ray diffraction (XRD) measurements on the sample obtained at 65 °C, to determine its chemical composition and crystal structure. As shown in Fig. 2, we found that the dark-blue sample was composed of three substances: one crystallized in a face-centered-cubic (FCC) phase with space group *Fm*-3*m* and lattice parameter a = 5.03 Å (henceforth referred to as "the FCC-1 phase"; see the peak positions indicated by the red vertical bars), which corresponds to LuH_2; the second also hosted a FCC unit cell (*Fm*-3*m*) with lattice parameter a = 4.755 Å (henceforth referred to as "the FCC-2 phase"; see the peak positions indicated by the green vertical bars); the third was determined to be the Lu hexagonal phase ($P6_3/mmc$) with lattice parameters a = 3.516 Å, b = 3.516 Å, and c = 5.57 Å (see the peak positions indicated by the blue vertical bars). The first two phases are recognized to be the same as the "hydride compounds A and B" described in Ref. 1. Although

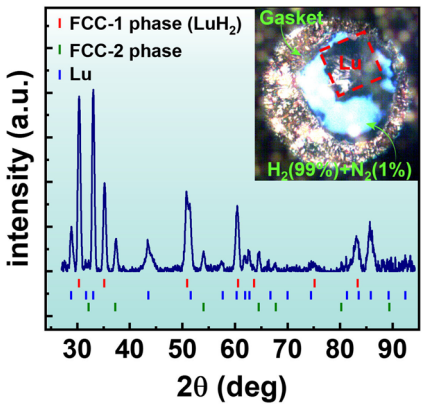

FIG. 2. XRD analysis of the sample obtained at 65 °C. All the diffraction peaks can be assigned to the FCC-1 phase (*Fm*-3*m*) with lattice parameter a = 5.03 Å (red bars), the FCC-2 phase (*Fm*-3*m*) with lattice parameter a = 4.755 Å (green bars), and the Lu metal (blue bars).

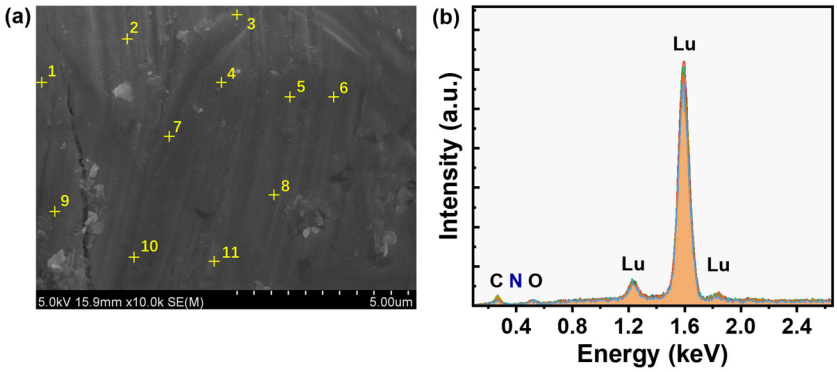

FIG. 3. Scanning electron microscopy (SEM) image and EDS analysis of the sample obtained at 65 °C. (a) SEM image taken from the produced sample surface. Eleven locations (marked by crosses) were selected to collect the EDS. (b) The overlay of the 11 EDS spectra measured shows that no nitrogen is incorporated in the sample.

Dasenbrock-Gammon *et al.*[1] did not mention the third substance, Lu metal, in their XRD work, it is reasonable to assume that unreacted Lu metal remained in the sample, because heating the sample to 65 °C and annealing it at this temperature for 24 h would not be able to complete the reaction between the lutetium foil and the gas mixture.

To determine the elemental composition of our sample, in particular the nitrogen content, energy-dispersive spectroscopy (EDS) measurements were carried out. As shown in Fig. 3, we measured 11 spots randomly on the sample obtained at 65 °C [Fig. 3(a)] and plotted the representative EDS spectra in Fig. 3(b). We did not find any trace of nitrogen incorporated in our sample. This absence of nitrogen in the sample may be attributed to the small amount of nitrogen (only 1%) in the gas mixture, which is too low to produce an effective reaction with the lutetium foil. In fact, recent studies on nitrogen-containing samples synthesized under high-pressure and high-temperature conditions have also found no superconductivity.[8,12] These results suggest that a small amount of nitrogen may not be crucial for producing superconductivity in the Lu-H-N sample.

As the heating temperature of 65 °C was not sufficient to make the lutetium foil react fully with the gas mixture (Fig. 2), we employed a laser heating technique to heat to 1800 °C another sample that had also been prepared using the gas mixture of hydrogen and nitrogen sources, and we then performed high-pressure resistance measurements on this sample. As shown in Fig. 4(a), the produced sample (henceforth referred to as "the sample obtained at 1800 °C") exhibited metallic behavior over the temperature range down to 4 K for pressures ranging from 0.9 to 6.5 GPa. We therefore conclude that the sample obtained at 1800 °C was not superconducting under these conditions, and, in addition, we found that the color of the compressed sample stayed dark blue [Figs. 4(b) and 4(c)]. To determine the crystal structure of the laser-heated sample, we conducted XRD measurements on it. As shown in Fig. 4(d), the sample obtained at 1800 °C included three substances: LuH_2 (see the peak positions indicated by the red vertical bars), the FCC-2 phase (Fm-3m) with lattice parameter a = 4.755 Å (see the peak positions indicated by the green vertical bars), and hexagonal LuH_3 ($P6_3/mmc$) with lattice parameters a = 3.56 Å, b = 3.56 Å, and c = 6.41 Å (see the peak positions indicated by the blue vertical bars). No Lu metal was found in this sample. These results indicate that the increased reaction temperature favored a thorough chemical reaction of the lutetium foil with the gas mixture.

LuH_2 and LuH_3 phases have been reported with no superconducting behavior in the temperature range of 300 K down to 4 K under pressures up to 7.7 GPa for LuH_2[2] and 122 GPa for LuH_3,[17] respectively, whereas for elemental Lu, superconductivity emerges at extremely low temperature (~0.3 K) and 11 GPa.[18] The FCC-2 phase found in this study is also not superconducting under pressures below 6.5 GPa.

Finally, an interesting property of the room-temperature superconductor described by Dasenbrock-Gammon *et al.*[1] was that the superconductivity occurred only in the pink phase, which transitioned from the blue one in the pressure range 0.3–3 GPa. Although

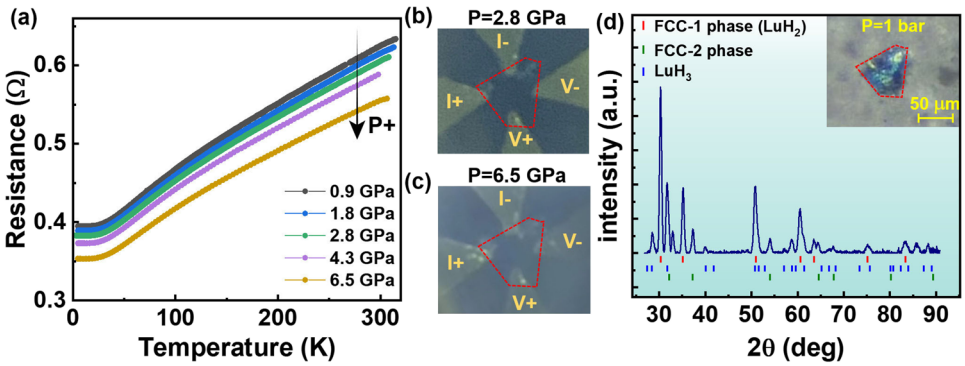

FIG. 4. Transport property and structural characterizations on the sample obtained at 1800 °C. (a) Temperature dependence of resistance measured at different pressures, displaying no evidence of superconductivity in the experimental range of 0.9–6.5 GPa. (b) and (c) Photographs taken at 2.8 and 6.5 GPa, demonstrating that the sample's color remains dark blue. (c) XRD pattern from the produced sample, revealing the presence of three substances: LuH_2 (red bars), FCC-2 phase (Fm-3m, green bars) and LuH_3 (blue bars).

we produced our samples employing the same method as that described in Ref. 1, we observed no color change in our two compressed samples (obtained at 65 and 1800 °C, respectively) below 3.4 and 6.5 GPa, respectively. Recent investigations have observed such a pink phase in nonsuperconducting Lu-H-N samples at pressures higher than ~11 GPa,[12,13] as well as in pure LuH_2 samples in the pressure range between ~2 and ~5 GPa.[2,4] Such a pressure-induced color change, which has been termed "piezochromism," is associated with an alteration of the bandgap and is often observed in plastics and semiconductors.[19,20] It would be interesting to investigate whether such materials with piezochromism can exhibit superconductivity.

In summary, we performed high-pressure investigations on two samples initially prepared by the same method as reported by Dasenbrock-Gammon *et al.*,[1] using a $99H_2/1N_2$ gas mixture and a lutetium foil as starting materials. One of the samples was then annealed at 65 °C for 24 h, as in Ref. 1, whereas the other was heated to 1800 °C for several minutes by a laser heating technique. High-pressure resistance and magnetic susceptibility measurements on the sample obtained at 65 °C did not show any evidence of superconductivity. The results of ambient-pressure XRD and EDS experiments on this sample revealed that it contained three substances: an FCC-1 phase (*Fm*-3*m*) that corresponds to LuH_2, an FCC-2 phase (*Fm*-3*m*), and hexagonal Lu metal ($P6_3/mmc$). The two FCC phases were identical to those found in the so-called near-ambient superconductor described in Ref. 1. No evidence of nitrogen incorporation in the sample obtained at 65 °C was found. Our high-pressure resistance measurements on the sample obtained at 1800 °C (the first lutetium hydride to be synthesized by this method) also found no evidence of superconductivity when the sample was cooled down to 4 K. XRD measurements showed that the sample obtained at 1800 °C consisted of a hexagonal LuH_3 phase ($P6_3/mmc$), the FCC-1 phase (*Fm*-3*m*), and the FCC-2 phase. Both samples remained dark blue in color at pressures below 6.5 GPa. These results of our investigation lead us to propose that the neither the sample prepared by the same method as that reported in Ref. 1 nor the sample synthesized by the laser heating method exhibited superconductivity in the near-ambient temperature and pressure ranges described in Ref. 1.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

S.C. and J.G. contributed equally to this paper.

L.S., T.X., Q.W., W.Y., and H.-K.M. designed the study and supervised the project. S.C., J.G., L.S., H.S., W.Y., and L.Y. prepared the samples. S.C. and L.S. performed the high-pressure resistance measurements. P.W., J.Z., and J.H. carried out high-pressure magnetic susceptivity measurements. S.C., L.S., and Y.Z. conducted SEM and EDS measurements. L.S., S.C., Q.W., and W.Y. wrote the manuscript in consultation with all the authors.

Shu Cai: Investigation (equal); Writing – original draft (equal). **Jing Guo**: Investigation (equal). **Haiyun Shu**: Investigation (equal). **Liuxiang Yang**: Investigation (equal). **Pengyu Wang**: Investigation (equal). **Yazhou Zhou**: Investigation (equal). **Jinyu Zhao**: Investigation (equal). **Jinyu Han**: Investigation (equal). **Qi Wu**: Investigation (equal); Supervision (equal); Writing – original draft (equal). **Wenge Yang**: Investigation (equal); Supervision (equal); Writing – review & editing (equal). **Tao Xiang**: Supervision (equal); Writing – review & editing (equal). **Ho-kwang Mao**: Supervision (equal); Writing – review & editing (equal). **Liling Sun**: Investigation (equal); Supervision (equal); Writing – original draft (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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