Reply to "Evidence of Superconductivity in Electrical Resistance Measurements of Hydrides Under High Pressure" by Balakirev et al

J. E. Hirsch
Department of Physics, University of California, San Diego, La Jolla, CA 92093-0319

In their Comment [1], Balakirev et al claim that our paper Ref. [2] that proposed an alternative explanation for resistance drops observed in many hydrides under pressure as the temperature is lowered interpreted as evidence for superconductivity, overlooked previously published experimental results that directly contradict its claims. Here we address the issues raised.

There have been many claims of high temperature superconductivity in hydrides under high pressure in recent years based on reported observation of large electrical resistance changes as function of temperature [3]. Measurements are performed with four electrodes in the van der Pauw (VDP) geometry. A large drop in resistance is seen at low temperatures and the observations are interpreted as meaning that the sample enters the superconducting state. Almost without exception, the results reported are for *resistance* rather than resistivity, because it is very difficult to infer resistivity values from measurements of very small inhomogeneous samples of uncertain dimensions and variable composition [4, 5].

In these measurements, a fixed current I is injected through two neighboring electrodes and the voltage drop V across the other two electrodes is measured, from which a resistance R=V/I is inferred, as shown in Fig. 1. By performing measurements with two alternative positions of the current and voltage electrodes, as shown in Fig. 1, two resistance values R_1 and R_2 are obtained. For a homogeneous quasi-two-dimensional sample of thickness d, van der Pauw showed [6] that the resistivity of the sample ρ satisfies the condition

$$e^{-\pi R_1 d/\rho} + e^{-\pi R_2 d/\rho} = 1 \qquad (1)$$

independent of the shape of the sample and of the position of the electrodes, from which the value of the resistivity can be extracted. For the particular case $R_1 = R_2 = R$, $\rho = \pi d R / ln2$.

In Ref. [2] we pointed out that the observations of

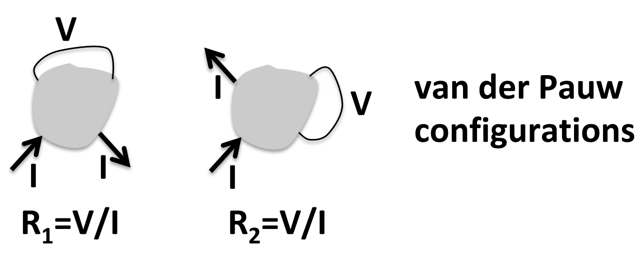

FIG. 1: The two van der Pauw electrode configurations from which the resistivity ρ can be extracted using Eq. (1) if the sample is homogeneous (there are two other equivalent ones obtained by interchanging current and voltage electrodes). If the sample is superconducting, both voltages will be zero and this implies $\rho = 0$.

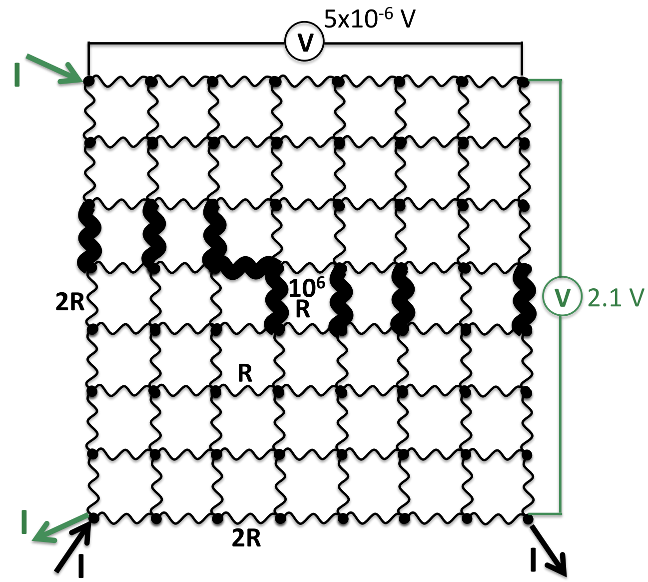

FIG. 2: Example of an inhomogeneous sample giving rise to near-zero voltage measurement, from Fig. 2 of Ref. [2]. The thin resistors have value $R = 1\Omega$, the thick resistors have value $10^6\Omega$. A current I=1A is injected and extracted. In green we show the alternative positioning of the van der Pauw electrodes, giving rise to a finite voltage and resistance.

near-zero voltage could result not from superconductivity but instead from the fact that at low temperatures certain regions of the inhomogeneous sample would become highly resistive, leading to near-zero voltage drop between the voltage electrodes without superconductivity. We modeled the system with a random resistor network, as shown in Fig. 2, assuming some of the resistances became very large at low temperatures. The results indicated that in a substantial fraction of the randomly generated samples, the measured voltage would decrease from finite values at high temperatures to near-zero values at low temperatures, which could be interpreted as meaning that the system was transitioning from a normal metallic state at high temperatures to a superconducting or highly conducting state at low temperatures, when in fact the exact opposite was happening. Fig. 2 shows one example of such a resistor configuration from our paper Ref. [2].

It may be asked why a two-dimensional model is ap-

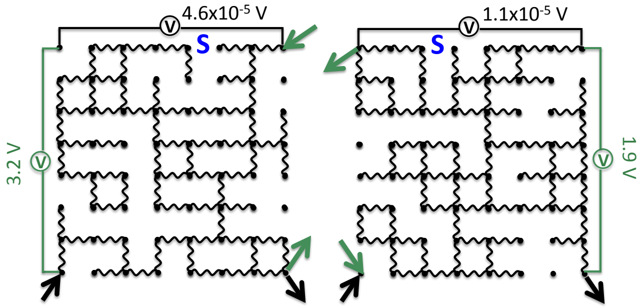

FIG. 3: Two examples of random configurations that suggest 'superconducting' behavior, from Fig. 6 of Ref. [2]. When switching the electrodes to the alternate VDP positions (green legends), the voltage does not diverge but remains finite. The values are indicated in the figure.

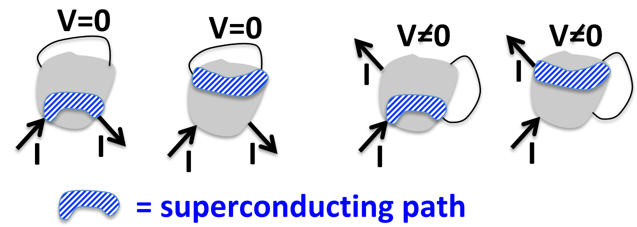

FIG. 4: A non-homogeneous sample with superconducting (dashed-blue) and metallic (grey) regions will yield zero voltage for two of the VDP electrode configurations and finite voltage for the other two, just as our random resistor network with no superconductivity Figs. 2 and 3.

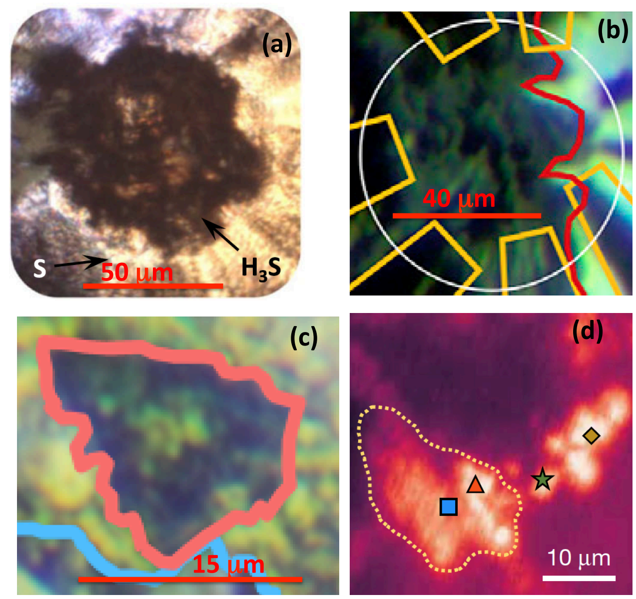

FIG. 5: Images of hydride samples under pressure reported to be superconducting below T_c. (a) H_3S at 155 GPa, from Fig. 1e of Ref. [8], $T_c \sim 196K$; (b) LaH_{10} at 180 GPa, from Fig. 1A of Ref. [13], $T_c \sim 550K$; (c) H_3S at 153 GPa, from Fig. 1 (f) of Ref. [14], $T_c \sim 197K$; (d) CeH_9 at 137 GPa from Fig. 4 d of Ref. [15], $T_c \sim 91K$.

propriate. The theoretical treatment by van der Pauw assumed "flat samples" [6], without specifying what that means. Experimental worked showed that van der Pauw's treatment holds for disk samples of height up to approximately 1/2 of their diameter [7]. The samples used in the hydride experiments are much flatter than that, typically of diameter $40\mu m$ to $80\mu m$ and thickness 1 to 3 μm [8, 9], so they should be well modelled by our two-dimensional resistor model, which reproduces the predictions of the van der Pauw treatment accurately [2]. We have not explored the effect of three-dimensionality which could become important for thicker samples.

The Comment of Balakirev et al [1] claims that in a situation such as shown in Fig. 2, yielding very small voltage, measuring with the alternative orientation of VDP electrodes *"would lead to divergence of the electrical resistance towards infinity"*. That claim is incorrect, as Fig. 2 shows with the green legends: when the current is injected and extracted through the left upper and lower corners, the voltage drop between the right upper and lower corners is 2.1V, not diverging, because there is a finite resistance path connecting the two current electrodes as the figure shows. Similarly in the two configurations labeled "S" in Fig. 6 of Ref. [2], shown here in Fig. 3, the voltage measured with one electrode configuration is of order 10^{-5}, suggesting 'superconductivity', and the one measured with the alternate electrode configuration is of order 1, not diverging, as shown in the figure. This is the generic behavior for the model proposed in our paper Ref. [2].

In nearly all the experimental papers in the literature reporting superconductivity in hydrides under pressure, measurements using only one electrode configuration are reported. If the authors of those papers also measured the alternative VDP electrode configuration and measured a finite resistance, presumably they concluded that because of inhomogeneity in the sample there was no superconducting path connecting the electrodes in the alternate configuration. This is illustrated in Fig. 4. This would be a valid conclusion *under the assumption that there is superconductivity in the sample*. However, the same observations would be explained with our model with no superconductivity, as shown in Figs. 2 and 3.

The samples used in the experiments searching for superconductivity in hydrides under high pressure are extremely inhomogeneous [4, 5, 10–12, 16]. Visual images of samples from four different experiments are shown in Fig. 5 to illustrate this. The patches believed to be superconducting extend only over regions sized a few microns, as for example Ref. [15] showed. Ref. [16] suggests that *"the hydride samples are probably porous and consist of microscopic grains ($\sim 0.05 - 0.5\mu m$)"*. Thus, the generic behavior that should be observed in transport experiments that claim to find superconducting samples (a substantial fraction of manufactured samples report-

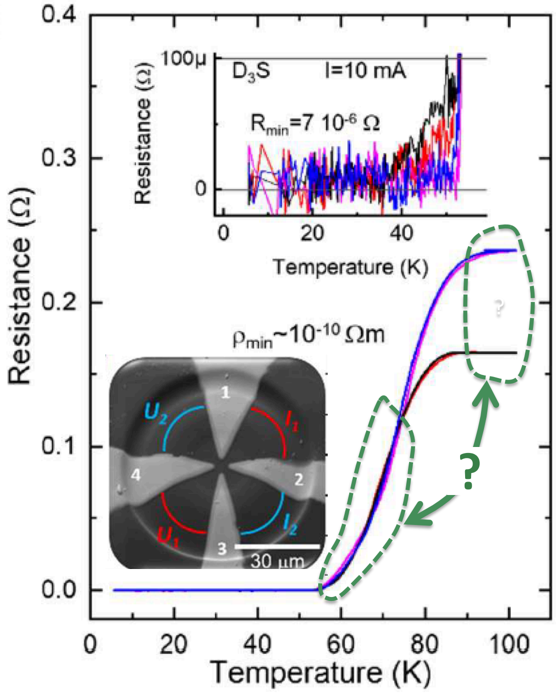

FIG. 6: Main body of the figure showing 4 resistance curves and upper inset reproduced from Fig. 1a of Ref. [1], lower inset showing electrode configurations reproduced from inset of Fig. 1(c) of Ref. [1], green markings added. It is unexpected that resistance curves for alternate electrode configurations would coincide in the region where resistances drop and not coincide at higher temperatures.

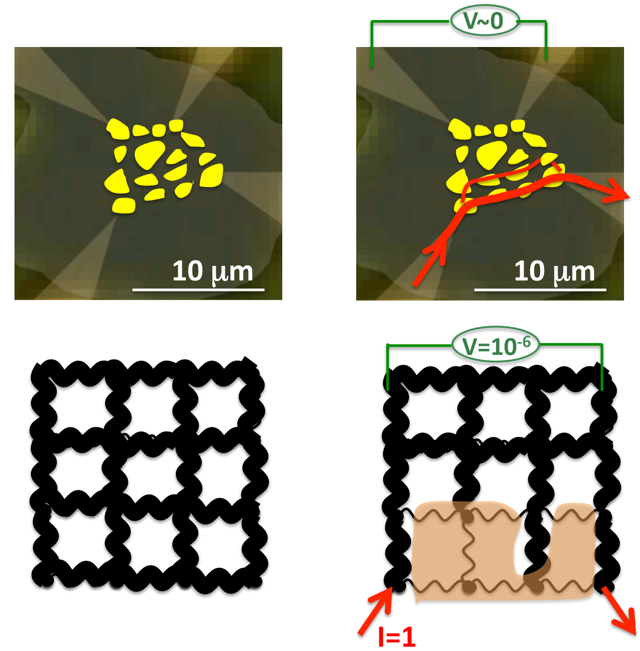

FIG. 7: Top panels: schematic depiction of an inhomogeneous sample, for which at low temperatures, the grains become disconnected from each other. In the lower panels this is represented by thick resistors assumed to have a value $10^6\Omega$. We hypothesize that when a current is applied, conducting filaments develop through which current flows, as discussed in Ref. [20]. Resistances in that region drop to much lower values, assumed here to be 1Ω (thin resistors), due to local heating indicated by the orange regions.

edly show no superconductivity at all) should be the one shown in Figs. 2, 3 and 4, i.e. zero resistance in one VDP configuration and finite resistance in the other. Thus, it is very strange that the authors of this Comment [1] claim that their experimental investigations *"consistently demostrate the vanishing resistance across all probe orientations"*. For some reason, inhomogeneous configurations of the type shown in Fig. 4, which should be common in these materials, do not show up in the experiments performed by the authors of Ref. [1]. This raises the possibility that the experiments performed by that group suffer from potential experimental artifacts.

Another peculiarity of the experiments reported by that group is seen in Fig. 1a of the Comment Ref. [1], from experiments performed in 2014 when the discovery of high temperature superconductivity in hydrides under pressure was first announced [9, 17]. The figure is reproduced here as Fig. 6. The alternative electrode configurations show two different values for the normal state resistance, presumably due to sample inhomogeneity. Yet when the resistance starts to drop, all the curves fall essentially on top of each other. This is completely unexpected for an inhomogeneous sample, and suggests that there may be experimental artifacts at play. The current paths go through regions of different resistance values at higher temperatures indicating inhomogeneity, and it is not expected that lowering the temperature somehow would make the sample more homogeneous. It should also be noted that Ref. [17] describes the measurements in Fig. 1a of Ref. [1] as *"R(T) measured with current of 10 mA at decreasing of temperature"*, while the figure caption of Fig. 1 of Ref. [1] states that the measurements were performed *"during slow warming"*. We discuss Fig. 6 further in the Appendix.

It remains to be explained: assuming that at least some of the experimental curves in Figs. 1 and 2 of the Comment showing near-zero resistance at low temperatures for all the VDP electrode configurations do not suffer from experimental artifacts, is there a possible explanation for these observations other than superconductivity?

We propose there is. Hydrogen-rich compounds under high pressure could be expected to undergo the prototypical Mott insulator-metal transition [18, 19], resulting from the competition between the intra-atomic Coulomb repulsion and the electronic hopping amplitude for electrons in neighboring hydrogen atoms. Other systems believed to undergo such transitions are vanadium oxides such as VO_2 and V_2O_3. In such systems, a sharp metal to insulator transition occurs as the temperature is lowered. We propose that certain properties of these "Mott materials" could explain some of the observations interpreted as superconductivity in the hydrides such as the resistance curves reported in Figs. 1 and 2 of the Comment Ref. [1], without superconductivity.

Indeed, as discussed in Ref. [20], when a voltage is applied to such materials in the low-temperature insulating state close to the insulator-metal transition, a conductive filamentary structure results through which current flows. As discussed in Ref. [20] and references therein, this results from the interplay of two mechanisms, namely Joule self-heating and hot carrier injection at strong electric fields resulting in collapse of the Mott gap. It leads to a current focusing effect and resulting conductive filament formation. The threshold voltage is consistently observed to be in the range of kV/cm in various materials [21]. Importantly, this resistive collapse is *"volatile"*, namely, when the voltage is removed the system returns to its original insulating state.

Consider for example the resistance curves in Fig. 1(a) of the Comment. At higher temperatures the resistance is approximately 0.2Ω. The current circulating is $10mA$, corresponding to a voltage drop of 2mV across the sample. For an intergrain distance of 20nm, the voltage across grains would be of order kV/cm, triggering the resistive collapse over the region of the sample close to where the current electrodes are, as shown schematically in Fig. 7. The voltage measured across the voltage electrodes would be near zero, as shown on the right panels of Fig. 7, suggesting superconductivity. The same would be seen for any orientation of the VDP electrodes for this sample if similar conducting filaments develop.

In summary we argue that resistance drops and measurement of near-zero voltages with van der Pauw electrodes in hydrides under pressure are not conclusive evidence of superconductivity, contrary to what the Comment claims. We certainly concur with the statement in the Comment *"we encourage the authors investigating superconductivity to measure and provide data on electrical resistance for claimed superconducting samples utilizing different patterns for the current-voltage probes."*, with the experimental protocol clearly stated. In addition, we would like to encourage authors to measure and provide resistance data obtained with a range of values of the applied current to support the inference that the measured resistance values reflect intrinsic properties of the samples not affected by the current itself.

Regarding the magnetic field dependence of the resistance drops observed, we suggest that there could be alternative explanations for it rather than superconductivity. For example, giant magnetoresistance has been reported for inhomogeneous semiconducting samples due to geometric effects [23], as well as for semiconductor-metal composites in the van der Pauw geometry [24, 25]. It would be interesting to explore the effect of varying the orientation of magnetic field with respect to the sample to distinguish between various possibilities. We also note that recent experiment on hydrides continue to show absence of resistance broadening with magnetic field [26], contrary to what is seen in standard superconductors, as we pointed out in earlier work [27]. Also, the presence or absence of hysteresis in magnetoresistance and other transport properties should be explored [28]: these materials are expected to be granular superconductors [10], for which hysteresis in transport properties with specific features is expected [28]. Finally, we hope that experimental protocols will be further refined to the point where different laboratories will be able to make samples using the same protocol that will exhibit resistance drops that closely resemble each other and are reproducible, and that the raw data for all measurements will consistently be made available.

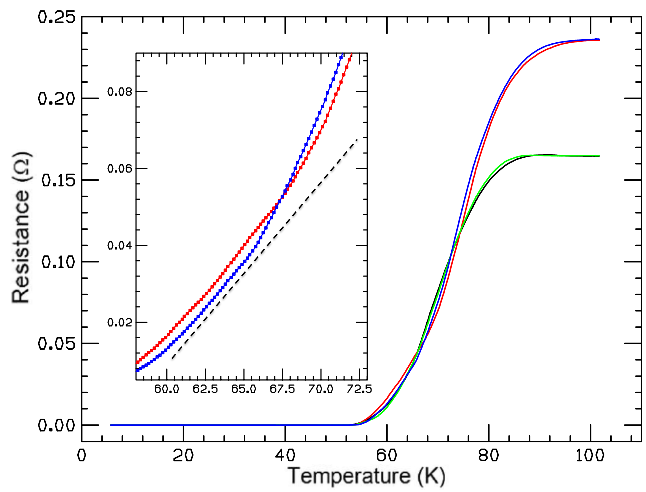

FIG. 8: Resistance curves of Fig. 6, from data provided by the authors of Ref. [1]. The inset shows the blue and red curves for part of the temperature range, the straight dashed line was added. Note the sharp change in slope of the blue curve around $T = 65.7K$, which is absent in the red curve

Appendix

Here we discuss further Fig. 6, reproduced from Fig. 1a of the Comment, originally published in Ref. [9]. Fig. 8 shows the same curves as Fig. 6, plotted using the raw data supplied with Ref. [1]. According to the Comment (caption of its Fig. 1), the protocol used for these measurements was:

"Measurements were conducted in four different orientations of the current-voltage probes (marked by different colors)…The current-voltage probes were changed every second during slow warming (1-2 kelvins per minute), allowing the recording of resistance values from four different channels within the same warming cycle. Any partial mismatch in R(T) values between different channels could be attributed to non-linear resistive responses in superconducting transition regions due to sample inhomogeneity. Panel a is reproduced from Ref. [3]…".

Since the red and blue curves in Fig. 8 coincide at the highest temperatures, as do the green and black curves, we infer that they correspond pairwise to the same VDP electrode configuration except for switching current and voltage contacts. The temperature intervals between successive points in the data files is approximately 0.175K. Since the warming rate was 1-2 kelvins per minute, this implies that the time interval between successive data points with the same electrode configuration was between 5 and 10 seconds. This is consistent with changing the current-voltage probes every second, as stated in the figure caption reproduced above, then waiting 1 to 6 seconds for the next set of measurements for the four electrode configurations. However, the data files show the same temperature values for the four electrode configurations at every point. Presumably this means that the authors took the temperature value for one of the electrode configurations and assigned the same value to the other 3 electrode configurations, even though the temperature had changed during the 4 seconds time interval that the electrode switching took place. Given this, we would expect the blue and red curves to be parallel and slightly shifted with respect to each other, and the same for the black and green curves, and the two pairs of curves to differ substantially from each other due to sample inhomogeneity, just as they do for temperature values above 80K.

What we see in Fig. 8 is very different and contrary to expectation. First, as mentioned earlier, the four curves are very close to each other in the region where the resistance is rapidly decreasing. Second, there are no parallel shifts, instead, the black and green curves cross each other, and so do the blue and red curves, in the region where the resistance is dropping. This is shown in the inset of Fig. 8 for the blue and red curves only for clarity. This cannot be due to time delay, under the reasonable assumption that the measurements at different temperatures occur in the same order. The curves show also the unusual feature that the slope of the blue curve changes sharply at temperature $\sim 65.7K$, while the slope of the red curve changes smoothly.

The figure caption in Ref. [1] attributes differences in resistance values between different channels to *"non-linear resistive responses" "due to sample inhomogeneity"*. It is true that a non-linear response could give rise to a difference between resistance measurements differing by interchanging current and voltage electrodes. However to explain Fig. 8 one would have to assume that inhomogeneity, non-linearity and time delay somehow combine to give rise to very similar curves for the four different electrode configurations, and cause a splitting in unexpected ways of curves that differ only by interchanging voltage and current electrodes that should be identical in the absence of nonlinearity.

Thus, we suggest that the data presented in Fig. 8 appear to be inconsistent with the described protocol. We also note that those were the only curves shown in the paper reporting the discovery of superconductivity in sulfur hydride [9] that showed resistance data under different VDP electrode configurations.

Acknowledgments

The author is grateful to M. Rozenberg for calling Ref. [20] to his attention and for helpful discussions.

---

[1] F. F. Balakirev, V. S. Minkov, A. P. Drozdov and M. I. Eremets, "Evidence of Superconductivity in Electrical Resistance Measurements of Hydrides Under High Pressure", preceding Comment.

[2] J. E. Hirsch, "Electrical resistance of hydrides under high pressure: evidence of superconductivity or confirmation bias?", J Supercond Nov Magn 36, 1495 (2023).

[3] I. A. Troyan, D.V. Semenok, A. V. Sadakov, I. S. Lyubutin and V. M. Pudalov, "Progress, problems and prospects of room-temperature superconductivity", arXiv:2406.11344 (2024) and references therein.

[4] D. Laniel et al, "High-pressure synthesis of seven lanthanum hydrides with a significant variability of hydrogen content", Nat Commun 13, 6987 (2022).

[5] A. Aslandukova et al, "Diverse high-pressure chemistry in $Y - NH_3BH_3$ andY–paraffin oil systems", Science Advances 10, eadl5416, DOI: 10.1126/sciadv.adl5416 (2024).

[6] L. J. van der Pauw, "A method of measuring specific resistivity and Hall effect of flat samples of arbitrary shape", Philips. Res. Rep. 13, 1 (1958).

[7] C. Kasl and M. J. R. Hoch, "Effects of sample thickness on the van der Pauw technique for resistivity measurements", Rev. Sci. Instrum. 76, 033907 (2005).

[8] V. Minkov, et al, "Magnetic field screening in hydrogen-rich high-temperature superconductors", Nat Commun 13, 3194 (2022).

[9] A.P. Drozdov, M.I. Eremets, I. A.Troyan, V. Ksenofontov and S. I. Shylin, "Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system", Nature 525, 73-76 (2015).

[10] M. I. Eremets et al, "High-Temperature Superconductivity in Hydrides: Experimental Evidence and Details", J Supercond Nov Magn 35, 965–977 (2022).

[11] A. P. Drozdov et al, "Superconductivity at 250 K in lanthanum hydride under high pressures", Nature 569, 528–531 (2019).

[12] Z. Li et al, "Superconductivity above 200 K discovered in superhydrides of calcium", Nat Commun 13, 2863 (2022).

[13] A. D. Grockowiak et al., "Hot Hydride Superconductivity above 550 K", Front. Electron. Mater. 2, 837651 (2022).

[14] I. Osmond et al, "Clean-limit superconductivity in Im3m H_3S synthesized from sulfur and hydrogen donor ammonia borane", Phys. Rev. B 105, L220502 (2022).

[15] P. Bhattacharyya et al, "Imaging the Meissner effect in hydride superconductors using quantum sensors", Nature 627, 73 (2024).

[16] I. A. Troyan et al, "High-temperature superconductivity in hydrides", Phys. Usp. 65, 748 (2022).

[17] A.P. Drozdov, M. I. Eremets and I. A. Troyan, "Conventional superconductivity at 190 K at high pressures", arXiv:1412.0460 (2014).

[18] N. F. Mott, "The Basis of the Electron Theory of Metals, with Special Reference to the Transition Metals", Proc. Phys. Soc. A 62, 416 (1949).

[19] N. F. Mott, "Metal-Insulator Transition", Rev. Mod. Phys. 40, 677 (1968).

[20] R. Rocco, J. del Valle, H. Navarro, P. Salev, I. K. Schuller and M. Rozenberg, "Exponential Escape Rate of Filamentary Incubation in Mott Spiking Neurons", Phys. Rev. Applied 17, 024028 (2022).

[21] P. Stoliar et al, "Universal Electric-Field-Driven Resistive Transition in Narrow-Gap Mott Insulators", Advanced Materials 25, 3222 (2013).

[22] J. E. Hirsch, "Are hydrides under high pressure high temperature superconductors?", National Science Review, nwad174 (2023) and references therein.

[23] T. Thio and S. A. Solin, "Giant magnetoresistance enhancement in inhomogeneous semiconductors", Appl. Phys. Lett. 72, 3497–3499 (1998).

[24] S. A. Solin et al, "Enhanced Room-Temperature Geometric Magnetoresistance in Inhomogeneous Narrow-Gap Semiconductors", Science 289, 1530 (2000).

[25] T. Zhou, S.A. Solin and D.R. Hines, "Extraordinary magnetoresistance of a semiconductor-metal composite van der Pauw disk", Journal of Magnetism and Magnetic Materials, 226–230, 1976 (2001).

[26] S. Cross et al, "High-temperature superconductivity in La_4H_{23} below 100 GPa", Phys. Rev. B 109, L020503 (2024).

[27] J. E. Hirsch and F. Marsiglio, "Nonstandard superconductivity or no superconductivity in hydrides under high pressure", Phys. Rev. B 103, 134505 (2021).

[28] J. E. Hirsch, "Granular superconductivity in hydrides under pressure", J Supercond Nov Magn 35, 2731–2736 (2022).