Intrinsic hysteresis in the presumed superconducting transition of hydrides under high pressure

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Superconducting transitions in the absence of magnetic field should be non-hysteretic. Here we address the fact that the drops in electrical resistance that have been interpreted as evidence of superconductivity in several hydrides under high pressure (so-called “superhydrides”) show hysteresis. We argue that the experimental evidence shows that the observed hysteresis cannot be attributed to experimental artifacts but is intrinsic to the samples. Assuming that the drops in resistance signal a thermodynamic phase transition, we argue that the presence of intrinsic thermal hysteresis indicates that these are first order transitions, whereas for standard superconductors the transition in the absence of applied magnetic field is always second order. We conclude that this is another feature that qualitatively distinguishes superhydrides from standard superconductors, in addition to the ones that have been pointed out earlier [1, 2], assuming these materials are superconductors. Alternatively and more likely, whether or not the drops in resistance signal a thermodynamic phase transition, our analysis indicates that superhydrides are not superconductors.

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I. INTRODUCTION

In several recent papers reporting findings of superconductivity under high pressure in hydrogen-rich compounds (generally called “superhydrides” [3]), resistance versus temperature data both in the absence and in the presence of applied magnetic field show hysteresis [4–8] [9]. Other findings of superconductivity in superhydrides did not inform whether or not hysteresis was checked for [10–20]. In this paper we point out that the experimental evidence indicates that the observed thermal hysteresis is intrinsic to the samples, rather than being due to experimental conditions. Assuming this is so, we argue that this is incompatible with standard superconductivity [21]. This then allows for one of two conclusions: (1) These materials are nonstandard superconductors [1], qualitatively different from both conventional and unconventional standard superconductors [22]; (2) These materials are not superconductors. We argue that the second alternative is far more likely.

II. EXPERIMENTAL EVIDENCE

We focus on the superconducting transition in the absence of a magnetic field. In standard superconductors this is a second order phase transition where no hysteresis can occur.

In the first paper where superconductivity was discovered in this class of materials [10], sulfur hydride, no evidence of thermal hysteresis appears. The paper does not inform whether the reported resistance versus temperature data were obtained on heating or cooling. Later studies on sulfur hydride did not address this issue either [11].

The recent paper where room temperature superconductivity of a carbonaceous sulfur hydride was reported [19] informs that the resistive transitions reported were all obtained upon heating the samples, and no information on the transition upon cooling or hysteresis is given.

In Fig. 1 we show schematically a typical thermal hysteresis loop for materials that show hysteresis. We call “direct hysteresis” when the drop of resistance upon cooling occurs at a lower temperature than the rise of resis-
tance upon heating, and ‘inverse hysteresis’ the reverse situation. Direct hysteresis would be expected if the transition is first order, so on cooling, the system supercools and in heating, it superheats before undergoing the transition.

The paper where high temperature superconductivity in lanthanum hydride was first reported [4] shows a hysteretic transition in its Fig. 3, with the drop of resistance upon cooling occurring at a higher temperature, by approximately 7 K, than the rise of resistance upon heating, i.e. what we call inverse hysteresis. Unfortunately the paper does not specify at which rate the heating and cooling was done.

The paper [4] informs that the sequence followed was to start at high temperatures (300K), cool down to 150K, and subsequently heat up to 300K again [4]. It is also notable that the normal state resistance did not return to its original value upon heating; instead it reached a value approximately 25% lower. In addition, the paper reports that the initial recorded pressure at 300 K was 188 GPa, and after the thermal cycle it was 196 GPa, without any change in the externally applied pressure. Finally, the paper reports that the resistance drop in the transition was a factor 2, 500.

In the same paper in Fig. S4 resistance versus temperature for several thermal cycles is shown, with varying pressure values (190 GPa, 202 GPa and 195 GPa) measured after each cycling, and the transition temperatures varying over a range of approximately 50 K. Also the resistance didn’t reach zero in these runs, and a subtraction was made to account for an assumed ‘contact resistance’.

These carefully reported experimental results [4] clearly inform the reader that upon changing the temperature, irreversible changes in the sample being studied occurred. How can we be sure that the resistance drops themselves are not also such an irreversible change? The transition between normal and superconducting states in standard superconductors, whether conventional or unconventional, whether type I or type II, in the absence of magnetic fields, is a second order reversible phase transformation [21]. The authors of Ref. [4] did not suggest any possible explanation for the hysteresis found in their experiments.

A second report of superconductivity in lanthanum hydride was given in Ref. [5]. Fig. 2 in that paper shows clear thermal hysteresis in the resistive transition in the absence of magnetic field, however there it is of the direct type (lower transition temperature upon cooling) in contrast to Ref. [4], with a hysteresis gap of approximately 3.5 K. The paper attributes the observed hysteresis to the “thermal mass of the pressure cell”, and reports that the rate of change of temperature upon heating was 0.2 K/min, but does not inform on the rate of temperature change upon cooling, nor on whether cooling or heating occurred first.

In Ref. [6], superconductivity in cerium superhydrides was reported. Here, both direct and inverse thermal hysteresis was reported, in Figs. S13 and S20 (inverse) and Fig. S30 (direct). In Fig. 1d hysteresis is also displayed but the paper does not specify which curve corresponds to cooling and which to heating. The hysteresis gap is ~ 0.6 K in Fig. S13, ~ 1 K in Fig. S20, and ~ 5 K, ~ 11 K and ~ 14 K in the various cases shown in Fig. S30. The rate of temperature change is reported to be 1 K/min in one case, and we assume it was the same in all cases. In several cases the resistance shown drops but remains finite on the low temperature side.

Upon questioning what could be the explanation that in some cases direct hysteresis and in other cases inverse hysteresis was found, the authors of [6] informed [23] that there were two different heaters in the experimental setup, and different controlling ways in different experiments would result in different results.

Ref. [7] also studied superconductivity in La superhydrides. Its Fig. 3 shows direct hysteresis, with a gap of about 8 K, with a reported rate of temperature change 0.7 K/min both in cooling and heating. The sequence was first cooling, then heating. The resistance drop at the assumed $T_c$ was not to zero but to approximately 10% of the normal state value. This was attributed [7] to either contact resistance of the leads or to a hypothesized ‘unreacted’ portion of the sample. The thermal hysteresis was attributed [7, 8, 24] to the fact that the temperature sensor was attached to the stainless steel frame of the diamond anvil cell, so it was hypothesized that the measured temperature was always ahead of the actual sample temperature.

Finally, in Ref. [8], the same authors of Ref. [7] reported superconductivity in Sn hydrides under high pressure. In their Fig. 3, they show a thermal hysteresis loop (direct hysteresis) of width ~ 5 K, obtained through first cooling and then heating, at a rate of about 0.3 K/min. The resistance drops by a factor of about 4, and this is assumed to be a superconducting transition, the finite low temperature resistance is attributed to an insufficient reaction of Sn with hydrogen. Note that the width of 5 K implies that it takes over 16 minutes to go from one to the other branch of the hysteresis loop. The authors attribute the thermal hysteresis to “an artifact originating from the different location of temperature sensor with respect to the sample.” [8]

In summary, in all of the existing reports of superconductivity in superhydrides detected through resistive transition to date, either no information on presence or absence of thermal hysteresis is given [10–20], or hysteresis is detected [4–8].

### III. INTRINSIC VS. NON-INTRINSIC HYSTERESIS

In the previous section we reviewed five papers where hysteretic resistive transitions for superhydrides were reported. In all the cases where explanations were suggested [5–8], the authors hypothesized that the hysteresis was an artifact of the experiment originating in the
fact that the temperature sensor was spatially separated from the sample, and that the change in temperature occurred at a finite rate rather than infinitely slowly. Let us examine this possibility.

Figure 2 shows a typical experimental setup, similar to the ones used in Refs. [6] [23] and [7, 8] [24]. The heater(s) (one or more), temperature sensor and sample are all in different locations. Cooling occurs through insertion of cold He gas. Depending on the geometry and the experimental protocol, it is possible that the sample could be temporarily at higher or lower temperature than the thermometer, both upon cooling or heating. If the hysteresis is an experimental artifact resulting from absence of thermal equilibrium, the degree of hysteresis should become smaller for a smaller rate of change in temperature and vanish for sufficiently slow rate. None of the experimental papers reports such checks. Nevertheless we argue that from the experimental information given it is possible to categorically reject this possibility.

Let us focus on the results reported in Ref. [8] for Sn hydrides for definiteness. The temperature where the resistivity begins to drop upon cooling (see Fig. 1 for temperature labels) is approximately $T_1 = 70.0K$, the corresponding point upon heating is $T_3 = 75.2K$. Similarly if we look at the temperatures where the resistance levels off after dropping, they are $T_2 = 68.4K$ and $T_4 = 73.4K$ respectively. Therefore, the width of the transition is approximately $\Delta T = T_1 - T_2 = T_3 - T_4 \approx 1.4K$ and the hysteresis gap is $\Delta T = T_3 - T_1 \approx T_4 - T_2 \approx 5K$. Let us assume, following the hypothesized qualitative explanation of these results by the authors of Ref. [8] [24], that the true transition occurs at the midpoint of the hysteresis loop, i.e. $T_c = 72.6K$ where the resistivity begins to drop, and that the hysteresis loop arises from the absence of thermal equilibrium between different parts of the experimental setup.

We argue that this explanation is not tenable because the rate of temperature change used in this experiment, $0.3K/min$, is orders of magnitude slower than would be required to explain the temperature imbalances implied by the numbers given above.

Consider for example the cooling process. How long after the temperature of the thermometer shows 72.6K, the true transition temperature, should we expect the sample to reach that temperature? At the cooling rate $0.3K/min$, the experiment tells us it took

$$\Delta t \sim \frac{2.6K}{0.3K/min} \sim 8.66\text{min} \sim 520s,$$

(1)

since at that time the thermometer showed $T_1 = 70.0K$ and the resistance began to drop. Let us estimate the true value of $\Delta t$.

We assume the dimensions of the sample were [8] $2\mu m \times 10\mu m \times 50\mu m$, with volume $V = 10^{-15}m^3$. The volumetric heat capacity of solids is approximately $C \sim 3MJ/m^3K$, so to change the temperature of the sample by $\Delta T$ requires an amount of heat

$$\Delta Q = CV\Delta T = 3 \times 10^{-9}J\Delta T(K).$$

(2)

We can estimate the time to transfer that heat between the sample and the thermometer from Fourier’s law $q = -\kappa \Delta T/L$ where $L$ is the distance between the two points, $\kappa$ the thermal conductivity of the medium conducting the heat, and $q = \Delta Q/(\Delta t)$ the heat flowing per unit area per unit time. Taking $A \approx 100(\mu m)^2$ as the cross-sectional area of the sample, $\kappa \sim 50W/(mK)$ the thermal conductivity of stainless steel, and $L \sim 10cm$ as an upper bound yields

$$\Delta t \sim \frac{CVL}{\kappa A} \sim 0.06s.$$

(3)

This calculation indicates that if the sample was at a higher temperature when the thermometer measured 72.6K in the process of cooling, it would have cooled to 72.6K in approximately 0.06s, rather than in 520s. Alternatively, we find for the difference in temperature between the sample and the thermometer

$$\Delta T = \frac{CVL dT}{\kappa A dt}$$

(4)

which for cooling rate $dT/dt = 0.3K/min$ yields $\Delta T = 0.003K$ instead of 2.6K, if the hysteresis gap originated in the finite rate of temperature change rather than being intrinsic. If we assume instead that the dominant thermal conductivity is that of diamond, which is substantially higher than that of stainless steel, this would give an even larger discrepancy.

In the other experimental papers where thermal hysteresis was reported the rate of change of temperature was similar, 0.2K/min in [5], 1K/min in [6] and 0.7K/min in [7]. It is clear that in no case can the hysteresis gap be attributed to the finite rate of temperature change and finite rate of heat conduction in the experimental apparatus, as was suggested in Refs. [5–8].
We conclude that the observed thermal hysteresis is intrinsic to the samples. This implies that the observed drops (and rises) in resistance cannot be solely due to the standard second order phase transitions between normal and superconducting states, as assumed in all the experimental as well as almost all the theoretical papers on these materials published to date.

IV. POSSIBLE EXPLANATIONS FOR THE OBSERVED HYSTERESIS

Hysteresis implies that an irreversible process is taking place. It cannot happen in second order phase transitions, but it can happen in first order phase transitions, depending on the situation and the rate of change of temperature. For example, for type I superconductors in a magnetic field the transition is thermodynamically reversible if the temperature or the magnetic field are changed sufficiently slowly. However, a system can be supercooled as well as slightly superheated due to the positive surface energy of the boundary between superconducting and normal phases [25], and will undergo an irreversible transition at a finite rate when it changes its phase at a temperature lower or higher than the critical temperature at the given magnetic field. The degree of supercooling and superheating will depend on details such as sample geometry and purity. The situation is even more complicated when the intermediate state is present [26]. Similarly, in the liquid-gas or liquid-solid transition there can be supercooling and superheating to varying degrees depending on the presence of nucleation sites, giving rise to thermal hysteresis.

However, because both direct [5–8] and inverse [4, 6] hysteresis have been observed in superhydrides as discussed in Sect. II, the hypothesis that the transition is a first order phase transition is not tenable since in first order phase transitions only direct hysteresis is seen. This would imply that if these are thermodynamic phase transitions they would be of a novel kind, neither standard first nor second order transitions, that would allow for both direct and inverse hysteresis. Or alternatively, the observation of inverse hysteresis could be due to experimental errors. We discuss the possibility of a first order phase transition further in the next section.

Alternatively and more likely, we have to consider the possibility that the drops and rises in resistance observed are not signatures of a thermodynamic phase transition, neither first nor second order. Rather, they may result from local rearrangements of atoms giving rise to conduction paths or breaking conduction paths as the temperature is decreased or increased. Such processes may occur at random and yield nonreproducible results in different runs under the same experimental conditions.

The inherent irreversibility of these experiments is also illustrated by the fact that the pressure measured at the same temperature after a thermal cycle is different than before the thermal cycle [4]. This indicates that irreversible changes occur during the thermal cycle.

More generally, the issue of irreproducibility has been pervasive in these experiments and needs to be addressed. Often, experiments done in different labs under reportedly similar conditions yield different results. It is important that experimental conditions are such that reproducible results can be achieved. Frequently it is stated in the experimental papers that different phases of the system may be close in energy configuration space, so the system may randomly adopt one or the other in irreproducible ways. Yet it is also assumed that in each of those hypothesized phases, a standard superconducting transition occurs. Usually this assumption is made largely based on the fact that theoretical calculations predict the transitions to occur.

Instead, we suggest that based on the experimental evidence, the inference that a superconducting transition is taking place is not warranted. If irreversible phenomena involving local atomic displacements or transitions between different structural phases of the material that are close in energy are taking place, they would also give rise to drops or increases in resistance, which could account for the observed phenomena.

V. A FIRST ORDER PHASE TRANSITION?

As discussed in the previous section, the first possibility that comes to mind when an apparent phase transition shows thermal hysteresis (of the direct type) is that it is a first order phase transition.

As is well known, the standard superconducting transition in the absence of a magnetic field is of second order and can be described by the Ginzburg Landau free energy density [21]

\[ f = f_n + \frac{\alpha}{\beta} |\psi|^2 + \frac{\beta}{\beta} |\psi|^4, \]  

where \( \psi \equiv |\psi| e^{i\theta} \) is a complex order parameter, \( \alpha \) and \( \beta \) are coefficients, and \( f_n \) is the normal state free energy density, when the order parameter is zero. Hereafter we will use \( \Delta \equiv |\psi| \) to simplify the expressions, as the phase, \( \theta \), does not enter in what follows. This simplified expression for the free energy density is valid in zero magnetic field and for a homogeneous order parameter.

For stability reasons the parameter \( \beta \) is assumed to be positive and temperature-independent. For \( \alpha > 0 \) the free energy is minimized by \( \Delta = 0 \), while for \( \alpha < 0 \) \( \Delta = -\alpha/\beta \) minimizes the energy. We can Taylor-expand the parameter \( \alpha \) around the temperature at which this sign change occurs \( T_c \), so \( \alpha \approx a_0 (T - T_c) \), and \( a_0 \) is a positive constant. From this we arrive at a mean-field description of the order parameter, which increases below \( T_c \) according to \( \Delta \propto \sqrt{(T_c - T)} \). This standard phenomenological description of superconductivity describes a continuous (second order) phase transition. Such a description seems to be ruled out by the evidence for ther-
for various temperatures, as dictated by differing choices of $\alpha$, as indicated in the legend. The highest temperature is for $\alpha_1 = 1$ and progresses downwards towards $\alpha_9 = -0.125$. Note that hysteresis may arise because, on lowering the temperature from $\alpha_4$ to $\alpha_5$ the system may choose to remain in the $\Delta = 0$ state. Only when the temperature is lowered to $\alpha_7$ (when $\Delta = 0$ is no longer a local minimum), does the system have to transition to a state with non-zero $\Delta$ (we show the negative solutions only as square points for clarity), at which point the resistance would drop to zero. Upon increasing the temperature, a similar phenomenon may occur, whereby the non-zero $\Delta$ state remains, until finally $\alpha_2$ is reached, and then a transition has to occur to the $\Delta = 0$ state with finite resistance.

We have pointed out in this paper that the thermal hysteresis observed in the resistive transition of superhydrides in the absence of a magnetic field is not an experimental artifact, as assumed in the literature [5–8], and instead is incompatible with these materials being standard superconductors. In standard superconductors, hysteresis in the resistive transition can exist only in the presence of a magnetic field in type I [25] as well as in type II superconductors, as was observed for example in Ref. [28]. In the absence of magnetic field, hysteresis has never been observed in standard superconductors, and would be in violation of the standard theory of superconductivity [21].

Therefore, if superhydrides are superconductors they are nonstandard superconductors. Thermal hysteresis in the absence of a magnetic field is yet another nonstandard property, in addition to the several ones pointed out earlier [1], that distinguishes superhydride superconductors from standard superconductors. The Ginzburg-Landau free energy, which has a universal form for standard superconductors, has to be qualitatively different for nonstandard superconductors, as discussed in Sect. V. Its precise form and physical justification remain to be determined.

If the superconducting transition in the superhydrides is first order, it is likely to be associated with a coupling of electronic degrees of freedom with lattice degrees of freedom, and give rise to a structural transformation together with the electronic transition. We are not aware of any such example in standard superconductors. However, such situations can exist in magnetic transitions that are ordinarily second order but become first order when lattice degrees of freedom are also involved [31], as well as in metal-insulator transitions such as in vanadium oxides [32]. Of course a metal-insulator transition coupled to lattice degrees of freedom could also explain the drops in resistance without any involvement of superconductivity. This possibility was suggested by Dogan and Cohen [2].

Given this situation, we argue that it is not warranted to calculate critical temperatures and other properties of superhydrides using the standard conventional theory of superconductivity, as is universally done [33]. There is no reason to expect that the conventional theory would be applicable to these nonstandard superconductors, given their radically different macroscopic properties. If such calculations agreed with observations, this would be accidental and would not lend credence to experimental results. Conversely, if experimental results did not agree with such theory, this should not cast doubt on the experimental results.

More likely however, our analysis in this and earlier
papers [1] as well as that of others [2] suggests that superhydrides are not superconductors. If the drops in resistance are accompanied by atomic rearrangements or other such irreversible processes, there is no reason to assume that superconductivity is also involved, unless one can detect clear evidence of superconductivity in magnetic properties. We have argued [1, 34] that such evidence, ac magnetic susceptibility [19] and magnetic field expulsion [35] presented in some papers as evidence of superconductivity, is faulty. It has also been independently acknowledged that because of experimental limitations, existing evidence from ac susceptibility measurements is not compelling [36].

The standard superconducting transition involves the establishment of macroscopic phase coherence in the electronic degrees of freedom, with resulting phase rigidity over macroscopic distances, without a concomitant lattice transition. A key experimental proof of superconductivity is the possibility to sustain persistent currents. For example, a magnet placed above a dirty YBCO sample will hover above it forever as long as the material is kept below 90 K. We argue that none of the existing experiments in these materials to date provides any evidence that persistent currents can exist in “superhydrides”.

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[1] J. E. Hirsch and F. Marsiglio, “Absence of high temperature superconductivity in hydrides under pressure”, arXiv:2010.10307 (2020); “Nonstandard superconductivity or no superconductivity in hydrides under high pressure”, arXiv:2012.12796 (2020); “Meissner effect in nonstandard superconductors”, arXiv:2101.01701 (2021).
[2] M. Dogan and M. L. Cohen, “Anomalous behavior in high-pressure carbonaceous sulfur hydride”, arXiv:2012.10771 (2020).
[3] R. J. Hemley et al., “Road to Room-Temperature Superconductivity: Tc above 260 K in Lanthanum Superhydride under Pressure”, arXiv:1906.03462 (2018).
[4] M. Somayazulu et al., ‘Evidence for superconductivity above 260 K in lanthanum superhydride at megabar pressures’, Phys. Rev. Lett. 122, 027001 (2019).
[5] A.P. Drozdov et al., ‘Superconductivity at 250 K in lanthanum hydride under high pressures’, Nature 569, 528-531 (2019).
[6] W. Chen et al, “High-Temperature Superconductivity in Cerium Superhydrides”, arXiv:2101.01315 (2021).
[7] F. Hong et al, “Superconductivity of Lanthanum Superhydride Investigated Using the Standard Four-Probe Configuration under High Pressures”, Chin. Phys. Lett. 37, 107401 (2020).
[8] F. Hong et al, “Superconductivity at ~ 70 K in Tin Hydride SnH6 under High Pressure”, arXiv:2101.02846 (2021).
[9] D. Semenok, private communication to authors (2020).
[10] A.P. Drozdov, Eremets, M. I., Troyan, I. A., Ksenofontov, V. and Shylin, S. I., ‘Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system’, Nature 525, 73-76 (2015).
[11] H. Nakao et al, “Superconductivity of Pure H3S Synthesized from Elemental Sulfur and Hydrogen”, J. Phys. Soc. Jpn 88, 123701 (2019).
[12] A.P. Drozdov, M. I. Eremets and I. A. Troyan, “Superconductivity above 100 K in PH3 at high pressures”, arXiv:1508.06224 (2015).
[13] A. D. Grockowiak et al, “Hot Hydride Superconductivity above 550 K”, arXiv:2006.03004 (2020).
[14] P. P. Kong et al, “Superconductivity up to 243 K in yttrium hydrides under high pressure”, arXiv:1909.10482 (2019).
[15] Y. A. Troyan et al., “Anomalous high-temperature superconductivity in YH6”, arXiv:1908.01534 (2019).
[16] E. Snider et al, “Superconductivity to 262 kelvin via catalyzed hydrogenation of yttrium at high pressures”, arXiv:2012.13627 (2020).
[17] D. V. Semenok et al., “Superconductivity at 161 K in thorium hydride ThH10: Synthesis and properties”, Materials Today 33, 36-44 (2020).
[18] D. V. Semenok et al, “Superconductivity at 253 K in lanthanum-yttrium ternary hydrides”, arXiv:2012.04787 (2020).
[19] E. Snider et al., ‘Room-temperature superconductivity in a carbonaceous sulfur hydride’, Nature 586, 373 (2020).
[20] D. Sun et al, ”High-temperature superconductivity on the verge of a structural instability in lanthanum superhydride”, arXiv:2010.00160 (2020).
[21] M. Tinkham, “Introduction to superconductivity”, Second Edition, McGraw Hill, New York, 1996.
[22] Physica C Special Issue, “Superconducting Materials: Conventional, Unconventional and Undetermined. Dedicated to Theodore H. Geballe on the year of his 95th birthday”, ed. by J.E. Hirsch, M.B. Maple, F. Marsiglio, Vol. 514, p. 1-444 (2015).
[23] W. Chen, private communication to authors (2021).
[24] Z. X. Zhao, private communication to authors (2021).
[25] T.E. Faber, ‘Creation and Growth of Superconducting Nuclei’, Nature 164, 277 (1949); “The phase transition in superconductors I. Nucleation”, Proc. Roy. Soc. 214, 392 (1952).
[26] Ruslan Prozorov, Russell W. Giammetta, Anatolii A. Polianskii, and Garry K. Perkins, “Topological hysteresis in the intermediate state of type-I superconductors,” Phys. Rev. B72, 212508 (2005).
[27] See D. Arovas, UCSD, Course Notes for Thermodynamics and Statistical Mechanics. for a good pedagogical de-
cription of this and other Ginzburg-Landau free energies that describe first order transitions.

[28] T. Terashima et al, “Hysteretic superconducting resistive transition in \( \text{Ba}_{0.07}\text{K}_{0.93}\text{Fe}_2\text{As}_2 \)”, Phys. Rev. B 87, 184513 (2013).

[29] Y. Achiam and Y. Imry, “Phase transitions in systems with a coupling to a nonordering parameter”, Phys. Rev. B 12, 2768 (1975).

[30] V.L. Ginzburg and A.P. Levanyuk, “On Light Scattering Near Phase-Transition Points in the Solid State,” Phys. Lett. 47A, 345 (1974).

[31] See for example M. Hudl et al, “Thermodynamics around the first-order ferromagnetic phase transition of \( \text{Fe}_2\text{P} \) single crystals”, Phys. Rev. B 90, 144432 (2014) and references therein.

[32] See for example M. H. Lee et al, “Controlling Metal-Insulator Transitions in Vanadium Oxide Thin Films by Modifying Oxygen Stoichiometry”, ACS Appl. Mater. Interfaces, 13, 887 (2021) and references therein.

[33] C. J. Pickard, I. Errea and M. I. Eremets, “Superconducting Hydrides Under Pressure”, Ann. Rev. Cond. Matt. Phys. 11, pp 57-76 (2020) and references therein.

[34] J. E. Hirsch, “About the Pressure-Induced Superconducting State of Europium Metal at Low Temperatures”, Physica C doi.org/10.1016/j.physc.2020.1353805 (2020).

[35] I. Troyan et al, “Observation of superconductivity in hydrogen sulfide from nuclear resonant scattering”, Science 351, 1303 (2016).

[36] V. Struzhkin et al, “Superconductivity in La and Y hydrides: Remaining questions to experiment and theory”, Matter and Radiation at Extremes 5, 028201 (2020).