Granular superconductivity in hydrides under pressure

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It has been suggested that the measured magnetic properties of hydrides under pressure claimed to be high temperature superconductors indicate that the materials are granular superconductors. Such materials will show reduced or no magnetic field expulsion under field cooling, and will trap magnetic fields when the external magnetic field is removed. They will also exhibit hysteretic behavior in magnetoresistance and other transport properties. Here we point out that hysteresis in transport properties has never been reported for hydrides under pressure. Its presence, with the expected features, would indicate that the materials trap magnetic flux, hence that they can sustain persistent currents without dissipation, something that all superconductors can do. Conversely, its absence would indicate that these materials are not superconductors.

Keywords: granular superconductor; hydride superconductor; pressure; trapped flux; hysteresis; magnetoresistance; critical current

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I. INTRODUCTION

Hydride superconductors under high pressure are usually identified as such by measuring their resistance as function of temperature. Large drops [1] (and sometimes small drops [2, 3]) in resistance are readily interpreted as indicating superconductivity, particularly when it is expected that the material should be a high temperature superconductor due to an earlier theoretical prediction [4]. In that way, more than 15 different hydrides under pressure have been claimed to be high temperature superconductors in recent years [5–9].

On the other hand, magnetic evidence for superconductivity in pressurized hydrides has been scarce. Ac magnetic susceptibility measurements reported to provide evidence for superconductivity [10–12] have been questioned [13–16]. Measurement of magnetization under field cooling [1, 17, 18] show no evidence of flux expulsion [19]. Magnetization measurements under zero field cooling show widely different behavior in different runs [1, 17–19], and no direct evidence of diamagnetism exists due to the necessity to subtract a background signal. In addition, when interpreted according to the standard theory of superconductivity these measurements indicate [19] that the materials have much larger critical fields and smaller London penetration depths than expected for standard superconductors, whether conventional or unconventional. An experiment performed to detect magnetic field exclusion using nuclear resonant scattering [20, 21] has also been questioned [22, 23] and has never been repeated.

Detection of magnetic flux trapping would evidence that the materials can sustain persistent current, hence that they are superconductors. Flux trapping can be detected by cooling the material in a magnetic field, removing the applied magnetic field, and measuring a remnant magnetization that persists for a long time. We have proposed such experiments over a year ago [23], however no experimental results have so far been reported. We conjecture that this is so because of the difficulty in performing reliable magnetization experiments with the small samples necessitated by the high pressures. In this paper, we propose that flux trapping in hydrides under pressure should be readily detectable in transport experiments. Such experiments should be much easier to perform.

II. GRANULAR SUPERCONDUCTORS

Granular superconductors [24] are polycrystalline materials with microcrystalline grains that are coupled through weak links (Josephson junctions), that establish the superconducting long-range order throughout the material. The weak links are broken by magnetic fields that are smaller than the magnetic field necessary to suppress superconductivity within the crystalline grains. As a consequence, the lower critical field H_{c1} in such materials can be very small. Such materials exhibit reduced flux expulsion under field cooling, since the magnetic field remains trapped both in intergranular regions and by pinning centers inside the micrograins. They will also exhibit a remnant magnetization, indicating flux trapping, when they are cooled in an external magnetic field and then the magnetic field is removed.

A characteristic property of granular superconductors, particularly high T_c cuprates, is that they exhibit hysteresis in various transport properties, in particular magnetoresistance and critical current [25]. The physical origin of these effects is flux trapping in the intragranular and intergranular regions and is well understood [26–29]. Such measurements are reported for polycrystalline samples of high T_c cuprate superconductors [31–40], BaPbBiO [41], organic superconductors [42], MgB_2 [43, 44],

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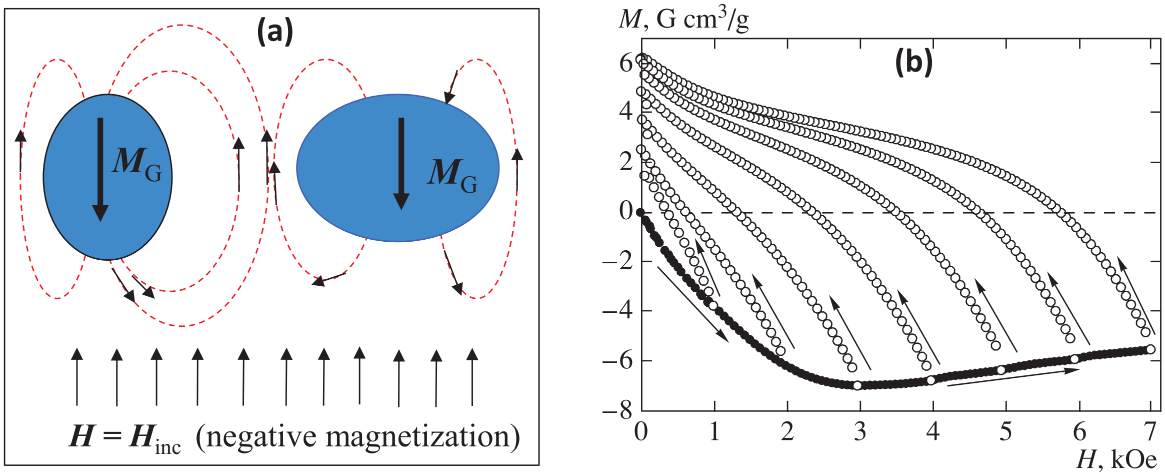

FIG. 1: (a): Intragrain magnetization M_G and resulting intergrain magnetic field (dashed red lines) when an increasing external magnetic field H is applied: the intergrain magnetic field is enhanced (the distance between grains is exaggerated for clarity). (b) Hysteresis cycle for the overall magnetization. (a) reproduced from ref. [25], (b) reproduced from ref. [26].

tungsten carbide [45], etc. Granularity can occur naturally in a polycrystalline sample due to the grain boundaries and can also be induced or enhanced by forming composites of the superconducting material and a non-superconducting material [26, 46–50]. For cuprate superconductors discovered in 1986, flux trapping was detected through magnetization measurements as early as 1987 [51], providing evidence for persistent currents, hysteresis in critical current was first measured in 1988 [50], and hysteresis in magnetoresistance in 1989 [31].

In ref. [18], Eremets et al argue that measurement of magnetic properties of hydride superconductors is elusive because of the "*granular or non-uniform distribution of the superconducting phase in samples*", and hence "*the electrical current finds a continuous path through superconducting grains and metallic grain boundaries in the transport measurements*" but the small size of the superconducting grains makes it difficult to detect magnetic signatures of superconductivity. Eremets et al [18] also argue that an anomalous peak in the resistance observed right before the drop in resistance interpreted as superconductivity results from the *"granular character of superconductivity"*, reflecting *"the non-uniformity of the superconducting phase in samples"*, just as in boron-doped diamond [52, 53], and that *"Importantly, not only the observation of zero resistance strongly supports superconductivity in hydrogen-rich compounds, but also the transition imperfections (broadening, steps, and peaks) discussed above, since these features are common among inhomogeneous superconductors."* The fact that hydrides are granular superconductors is also remarked by Semenok et al [7] and by Drozdov et al [54].

If hydrides under pressure are granular superconductors, they should exhibit transport properties characteristic of such superconductors, in particular hysteresis in magnetoresistance and in critical current. These properties would provide evidence that the materials trap magnetic flux and hence that persistent currents can flow in hydrides under pressure without dissipation, thus proving that the materials are indeed superconductors, disproving suggestions to the contrary [14, 19, 22, 23, 55]. No such hysteretic behavior in transport properties has been reported to date to our knowledge, for any of the more than 15 different hydrides under pressure claimed to be high temperature superconductors, for which extensive transport measurements have been reported [5–9]. We suggest that these experiments should be urgently performed. In order to enhance the granularity to make these effects more apparent, it should be possible to fabricate composite samples of a hydride and another material, as in other superconductors where these effects are clearly observed [26, 46–50].

III. TRANSPORT PROPERTIES OF GRANULAR SUPERCONDUCTORS

Here we discuss examples of transport properties of granular superconductors to illustrate behaviors that should be found in transport measurements of hydrides or hydride composites under pressure that are claimed to be high temperature superconductors.

Figure 1 illustrates the physics that explains the observed hysteretic behavior in transport properties [27]. When an increasing magnetic field is applied, it induces a negative magnetization inside the grains, which enhances the magnetic field in the inter-granular region (left panel). When the magnetic field is then decreased, the magnetization decreases and then changes sign (right panel), and the magnetic field in the intergranular region will consequently be reduced (as can be seen by flipping the arrows of magnetization and magnetic field lines in the left panel).

Both the resistance and the critical current are domi-

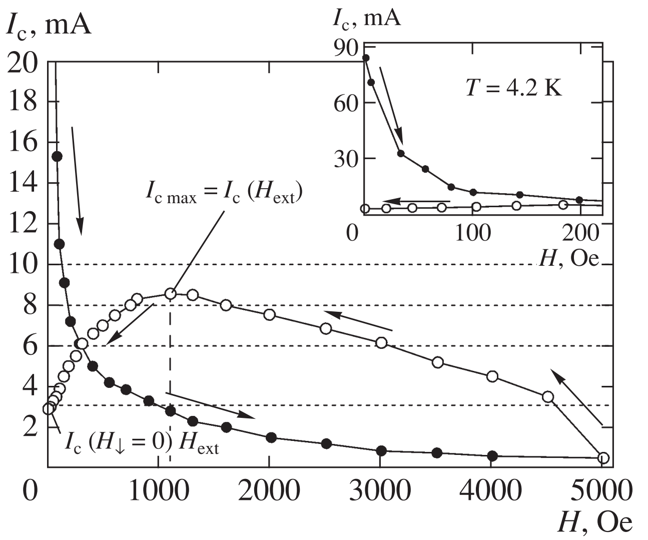

FIG. 2: Magnetic field dependence of critical current for a YBCO-CuO composite, reproduced from ref. [26]. The inset shows the behavior for weak fields. The arrows show the direction of change of the external magnetic field.

nantly determined by transport in the intergranular regions. Therefore, as a consequence of the physics discussed in the above paragraph, the resistance will be higher and the critical current will be lower when the magnetic field is increased versus when it is decreased.

Fig. 2 shows an example of critical current measurement illustrating the qualitative behavior described above. There are in addition other interesting features, in particular, in decreasing the external field the critical current reaches a maximum I_{cmax} and then decreases. This is explained in ref. [27] as arising from the fact hat at that point the effective field in the intergrain region is compensated to the largest extent, and upon further lowering of the applied field it increases, hence the critical current decreases. As the applied field reaches zero again the sample has a positive magnetic moment (fig.1 right panel) giving rise to magnetic field in the intergranular region, hence the critical current is smaller than before a field was applied.

Similarly, this physics explain the hysteretic behavior of the magnetoresistance shown in Fig. 3. Initially as the field is increased the intergranular magnetic field is enhanced, giving rise to larger resistance than in the return cycle when the applied magnetic field is decreased. The minimum and subsequent rise when the external field is further decreased is explained as the corresponding behavior for critical current discussed in the above paragraph. The degree of hysteresis depends on the magnitude of the current and the maximum value of the magnetic field, the temperature, and characteristics of the sample. It can be much smaller than what is shown for illustration in Fig. 3. Hysteresis is seen for a wide range of temperatures [56], ranging from close to T_c to low temperatures.

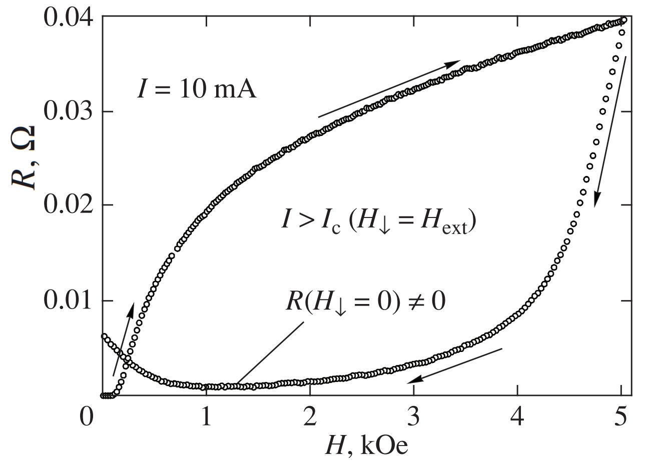

FIG. 3: Magnetic field dependence of resistance for a YBCO-CuO composite, reproduced from ref. [26]. The arrows show the direction of change of the external magnetic field.

Hysteretic behavior in other transport properties such as current noise [57] and surface resistance [58], originating in the same physics, has also been reported for granular superconductors and could be investigated for hydride superconductors.

Another consequence of the physics discussed here is that resistance and critical current depend on thermomagnetic history, because of flux trapping. In particular, resistance is lower and critical current is higher for field-cooled versus zero-field-cooled samples since the magnetic field in the intergranular region will be smaller for field-cooling due to the physics discussed above. This is observed in high T_c cuprates [59–62] and should be investigated for hydride superconductors.

IV. DISCUSSION

The figures shown in the previous section display *qualitatively* the expected hysteretic behavior in critical current and magnetoresistance expected for granular superconductors due to flux trapping. Depending on the degree of granularity and other specific features of the materials, various differences could arise. In particular, the width of the hysteresis loops could be much smaller. However, the qualitative features should remain. In particular, the hysteretic loops should always be clockwise for magnetoresistance (Fig. 3) and counterclockwise for critical current (Fig. 2). Of course there could be other spurious reasons for observed hysteresis unrelated to flux trapping, for example heating effects or irreversible structural changes, that would be sensitive to the rate at which parameters are changed, that need to be carefully considered and ruled out.

Observation of hysteretic behavior in transport properties qualitatively similar to what is shown in figs. 2 and 3, together with the expected dependence of transport properties on history (field-cooled vs. zero field cooled), would provide convincing proof that hydride superconductors trap magnetic flux, hence are superconductors. These measurements should be much easier to perform than magnetization or ac susceptibility measurements. Of course absence of such hysteretic behavior in transport properties could also be interpreted as signifying that the materials are superconductors but not granular. However that would be a difficult case to make, since granularity has been invoked to explain why these materials do not exhibit clearer features of superconductivity [18]. In addition, it should not be difficult to produce or enhance granularity in the samples by mixing in other components in the sample preparation to create hydride-metal or hydride-oxide composites, as is done for high T_c cuprates [26, 46, 47].

If experiments fail to detect hysteretic behavior of the type expected in transport properties for hydride samples that are granular materials, it would indicate that these materials don't trap magnetic flux. Given that other observed properties can only be explained if they do trap magnetic flux, such as the absence of field expulsion under field cooling [18] and the screening of magnetic fields larger than the lower critical field [20, 21], it would indicate that these materials are not superconductors. Hence that the observed drops in resistance are not due to superconductivity but due to other physics [63, 64], contrary to innumerable theoretical predictions based on the conventional theory of superconductivity that predict superconductivity in these materials [65]. This would cast serious doubt on the validity of the conventional theory to describe any superconducting material, and support the theory of hole superconductivity proposed as a description of superconductivity in all materials [55].

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[1] 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).
[2] H. Nakao et al, "Superconductivity of Pure H_3S Synthesized from Elemental Sulfur and Hydrogen", J. Phys. Soc. Jpn. 88, 123701 (2019).
[3] A. D. Grockowiak et al, "Hot Hydride Superconductivity Above 550K", Front. Electron. Mater, March 2022, Article 837651.
[4] D. Duan, Y. Liu, F. Tian, D. Li, X. Huang, Z. Zhao, H. Yu, B. Liu, W. Tian, and T. Cui, "Pressure-induced metallization of dense $(H_2S)_2H_2$ with high-T_c superconductivity", Sci. Rep. 4, 6968 (2014).
[5] D. Wang, Y. Ding and H. K. Mao, "Future Study of Dense Superconducting Hydrides at High Pressure", Materials 14, 7563 (2021) and references therein.
[6] Jingkai Bi et al, "Efficient route to achieve superconductivity improvement via substitutional La-Ce alloy superhydride at high pressure", arXiv:2204.04623 (2022).
[7] D. V. Semenok et al, "Effect of paramagnetic impurities on superconductivity in polyhydrides: s-wave order parameter in Nd-doped LaH_{10}", arXiv:2203.06500 (2022).
[8] L. Ma et al., "High-temperature superconducting phase in clathrate calcium hydride CaH_6 up to 215 K at a pressure of 172 GPa", Phys. Rev. Lett. 128, 167001 (2022).
[9] Changling Zhang et al, "Superconductivity in Zirconium Polyhydrides with Tc above 70K", arXiv:2112.14439 (2022).
[10] X. Huang et al, "High-temperature superconductivity in sulfur hydride evidenced by alternating-current magnetic susceptibility", Nat. Sci. Rev. 6, 713 (2019).
[11] V. Struzhkin et al, "Superconductivity in La and Y hydrides: Remaining questions to experiment and theory", Matter and Radiation at Extremes 5, 028201 (2020).
[12] E. Snider et al., "Room-temperature superconductivity in a carbonaceous sulfur hydride", Nature 586, 373 (2020).
[13] J. E. Hirsch, "Faulty evidence for superconductivity in ac magnetic susceptibility of sulfur hydride under pressure", arXiv:2109.08517 (2021).
[14] J. E. Hirsch and F. Marsiglio, "Absence of magnetic evidence for superconductivity in hydrides under high pressure", Physica C 584, 1353866 (2021).
[15] J. E. Hirsch, "Comment on "Room-temperature superconductivity in a carbonaceous sulfur hydrid" by Elliot Snider et al.", EPL 137, 36001 (2022).
[16] D. van der Marel and J. E. Hirsch, "Extended Comment on Nature 586, 373 (2020) by E. Snider et al", arXiv:2201.07686 (2022).
[17] V. S. Minkov et al, "The Meissner effect in high-temperature hydrogen-rich superconductors under high pressure", DOI:10.21203/rs.3.rs-936317/v1 (2021).
[18] M. I. Eremets et al, "High-temperature superconductivity in hydrides: experimental evidence and details", arXiv:2201.05137 (2022); J Supercond Nov Magn (2022) https://doi.org/10.1007/s10948-022-06148-1.
[19] J. E. Hirsch and F. Marsiglio, "Clear evidence against superconductivity in hydrides under high pressure", rXiv:2110.07568 (2021).
[20] I. Troyan et al, "Observation of superconductivity in hydrogen sulfide from nuclear resonant scattering", Science 351, 1303 (2016).
[21] R. Prozorov and S. L. Bud'ko, "On the analysis of the tin-inside-H3S Mössbauer experiment", arXiv:2204.07847 (2022).
[22] J. E. Hirsch and F. Marsiglio, "Meissner effect in nonstandard superconductors", Physica C 587, 1353896 (2021).
[23] J. E. Hirsch and F. Marsiglio, "Flux trapping in superconducting hydrides under high pressure", Physica C 589, 1353916 (2021).

[24] Guy Deutscher, "New Superconductors: From Granular to High T_c, World Scientific, Singapore, 2014.

[25] D. A. Balaev, S. V. Semenov and D. M. Gokhfeld, "New Evidence of Interaction Between Grain and Boundaries Subsystems in Granular High-Temperature Superconductors", J. Sup. Nov. Mag. 34, 1067 (2021) and references therein.

[26] D. A. Balaevet al, "Magnetoresistance Hysteresis in Granular HTSCs as a Manifestation of the Magnetic Flux Trapped by Superconducting Grains in YBCO + CuO Composites", J. Exp. Theor. Phys. 105, 11741183 (2007).

[27] D. A. Balaevet al, "Mechanism of the hysteretic behavior of the magnetoresistance of granular HTSCs: The universal nature of the width of the magnetoresistance hysteresis loop", J. Exp. Theor. Phys. 108, 241 (2009).

[28] I. Garca-Fornaris E. Govea-Alcaide, P. Mun and R. F. Jardim, "Magnetoresistance, transport noise and granular structure in polycrystalline superconductors", phys. stat. sol. (a) 204, 805 (2007).

[29] S. V. Semenov and D. A. Balaev, "Model of the Behavior of a Granular HTS in an External Magnetic Field: Temperature Evolution of the Magnetoresistance Hysteresis", Phys. Solid State 62, 1136 (2020).

[30] S. Shifang et al, "The Behaviour of Negative Magnetoresistance and Hysteresis in $YBa_2Cu_3O_{7-\delta}$", EPL 6, 359 (1988).

[31] Y. J.. Quian et al, "Transport hysteresis of the oxide superconductor $Y_1Ba_2Cu_3O_{7-x}$ in applied fields", Phys. Rev. B. 39, 4701 (1989).

[32] K. Y. Chen and Y. J. Qian, "Critical current and magnetoresistance hysteresis in polycrystalline $YBa_2Cu_3O_{7-x}$, Physica C 159, 131 (1989).

[33] A. K. Pradhan et al, "H_{c1} measurements using hysteresis in magnetoresistance of sintered YBaCuO", Applied Superconductivity 3, 223 (1995).

[34] I. Felner et al, "Magnetoresistance hysteresis and critical current density in granular $RuSr_2Gd_{2x}Ce_xCu_2O_{10-\delta}$, Phys. Rev. B 67, 134506 (2003).

[35] T. V. Sukhareva and V. A. Finkel, "Hysteresis of the Magnetoresistance of Granular HTSC $YBa_2Cu_3O_{7-\delta}$ in Weak Fields, Phys. Solid State 50, 1001 (2008).

[36] A. Das, A .Banerjee and R. Srinivasan, "History effects in low-field magnetoresistance of BPSSCO polycrystals", Bull. Mater. Sci. 17, 607 (1994).

[37] V. V. Derevyanko, T. V. Sukhareva and V. A. Finkel, "Magnetoresistance hysteresis of granular $YBa_2Cu_3O_{7-\delta}$ high-temperature superconductor in weak magnetic fields", Tech. Phys. 53, 321 (2008).

[38] S. V. Semenov, A. D. Balaev and D. A. Balaev, "Dissipation in granular high-temperature superconductors: New approach to describing the magnetoresistance hysteresis and the resistive transition in external magnetic fields", Journal of Applied Physics 125, 033903 (2019).

[39] D. A. Balaev et al, "Specific Features in the Hysteretic Behavior of the Magnetoresistance of Granular High Temperature Superconductors", Phys. Solid State 54, 2155 (2012).

[40] M.G. das Virgens, S. Garcia and L. Ghivelder, "Lower critical field and intragrain critical current density in the ruthenate-cuprate $RuSr_2Gd_{1.5}Ce_{0.5}Cu_2O_{10}$, Eur. Phys. J. B 49, 135 (2006).

[41] D. A. Balaev et al, "Nonmonotonic Behavior of Magnetoresistance, bR(H) Hysteresis, and Low Temperature Heat Capacity of the $BaPb_{0.75}Bi_{0.25}O_3$ Superconductor in a Magnetic Field: Possible Manifestations of Phase Separation", J. Exp. Theor. Phys. 110, 584 (2010).

[42] S. Sugiura et al, "Josephson vortex dynamics and Fulde-Ferrell-Larkin-Ovchinnikov superconductivity in the layered organic superconductor $\beta-(BEDT-TTF)_2SF_5CH_2CF_2SO_3$, Phys. Rev. B 100, 014515 (2019).

[43] M. Olutas et al, "Hysteresis Effects in Magnetovoltage Measurements in Superconducting MgB_2, : IEEE Transactions on Applied Superconductivity 19, 2744 (2009).

[44] M. Olutas, A. Kili, K. Kili and A. Altinkok, "Irreversibility Effects and Low Field Magnetovoltage Measurements in Superconducting MgB_2 Near the Critical Temperature T_c", J Supercond Nov Magn 26, 3369 (2013).

[45] J. Barzola-Quiquia et al, "Andreev Reflection and Granular Superconductivity Features Observed in Mesoscopic Samples Using Amorphous Tungsten Carbide Superconductors", J Supercond Nov Magn 24, 463 (2011).

[46] D.A. Balaev et al, "Magnetoresistance hysteresis of bulk textured $Bi_{1.8}Pb_{0.3}Sr_{1.9}Ca_2Cu_3O_x + Ag$ ceramics and its anisotropy", Physica C 470, 61 (2010).

[47] A. Altinkok, K. Kili, M. Olutas and A. Kili, "Magnetovoltage Measurements and Hysteresis Effects in Polycrystalline Superconducting $Y_1Ba_2Cu_3O_{7-x}/Ag$ in Weak Magnetic Fields", J Supercond Nov Magn 26, 3085(2013).

[48] H. Zhou and X. Jin, "Stray field and vortex controlled magnetoresistance in superconducting Bi/Ni bilayers", Journal of Magnetism and Magnetic Materials 458, 171 (2018).

[49] S. K. He et al, "Hysteresis magnetoresistance and edge superconductivity in Nb film with diluted square array of holes", Supercond. Sci. Technol. 30 115016 (2017).

[50] J.E. Evetts and B.A Glowacki, "Relation of critical current irreversibility to trapped flux and microstructure in polycrystalline $YBa_2Cu_3O_7$, Cryogenics 28, 641 (1988).

[51] K. A. Müller, M. Takashige and and J. G. Bednorz, "Flux Trapping and Superconductive Glass State in $La_2CuO_{4-y} : Ba$", Phys. Rev. Lett. 58, 1143 (1987).

[52] G. Zhang et al., "Bosonic Anomalies in Boron-Doped Polycrystalline Diamond", Phys. Rev. Appl., 064011 (2016).

[53] G. Zhang et al., "Metal-Bosonic Insulator-Superconductor Transition in Boron-Doped Granular Diamond", Phys. Rev. Lett, 077001 (2013).

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

[55] J. E. Hirsch, "Hole superconductivity xOr hot hydride superconductivity", Journal of Applied Physics 130, 181102 (2021).

[56] S. V. Semenov and D. A. Balaev, "Magnetoresistance Hysteresis Evolution in the Granular Y-Ba-Cu-O High-Temperature Superconductor in a Wide Temperature Range", J Supercond Nov Magn 32, 2409 (2019).

[57] M. Celasco et al, "Evidence of current-noise hysteresis in superconducting $YBa_2Cu_3O_{7?\delta}$ specimens in a magnetic field", Phys. Rev. B. 43, 11478 (1991).

[58] L. Ji, M. S. Rzchowski, N. Anand, and M. Tinkham, "Magnetic-field-dependent surface resistance and two-level critical-state model for granular superconductors", Phys. Rev. B 47, 470 (1993).

[59] P. K. Mishra et al, "Transport Critical Current Density of Polycrystalline YBCO in Zero Field Cooled and Field

 doi:10.20944/preprints202204.0251.v1

Cooled States: A Comparison", Jpn. J. Appl. Phys. 29 L1612 (1990).

[60] D Lopez and F de la Cruz, "Anisotropic energy dissipation in high-T_c ceramic superconductors: Local-field effects", Phys. Rev. B 43, 11478(R) (1991).

[61] D Lopez, R Decca and F de la Cruz, "Anisotropic energy dissipation, flux flow and topological pinning in ceramic superconductors", Supercond. Sci. Technol. 5, S276 (1992).

[62] D. A. Balaev et al, "General regularities of magnetoresistive effects in the polycrystalline yttrium and bismuth high-temperature superconductor systems", Phys. Solid State 53, 922 (2011).

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

[64] M. Dogan and M. L. Cohen, "Anomalous behavior in high-pressure carbonaceous sulfur hydride", Physica C 583, 1353851 (2021).

[65] L. Boeri et al, "The 2021 Room-Temperature Superconductivity Roadmap", J. Phys. Cond. Matt. 34, 183002 (2022) and references therein.