Electrical resistance of hydrides under high pressure: evidence of superconductivity or confirmation bias?

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During the past 9 years, extensive experimental evidence has been presented that is claimed to demonstrate that hydrogen-rich materials under high pressure are high temperature superconductors, as predicted by conventional BCS-electron-phonon theory. Foremost among the experimental evidence are electrical resistance measurements, claimed to show that the resistivity of these materials falls well below that of the best normal metals within experimental accuracy. Here I propose an alternative explanation for the vanishingly small resistance reported for these materials that does not involve superconductivity.

There are by now at least 15 hydrogen-rich materials that have been reported to be high temperature superconductors under high pressure [1] starting in the year 2014 [2, 3]. They all have in common that resistance is measured in diamond anvil cells (DAC's) for very small samples, and that the precise location of hydrogen atoms in the structures is unknown. They also have in common that experiments don't exactly reproduce, even in the same laboratory for the same samples, when measurements are repeated. It is often stated that samples are inhomogeneous [4–6], that several different phases may coexist in the same sample [7], that samples are granular [1, 4, 5] and that not all the material in the region of the sample holder may be in superconducting phase(s), since portions of non-superconducting precursor material may remain after the fabrication process involving laser heating [4, 8]. Measurements claiming very small or zero resistance within experimental error are performed using the Van der Pauw four-probe methodology [9]. Sometimes measurements with three probes are reported that show finite resistance (usually large) that is attributed to 'contact resistance' [10–13]. Usually in these reports no attempts are made to extract resistivity from resistance measurements, due to uncertainty in the geometry and composition of the samples. Finally, what is common to all this work is that invariably it is emphasized that the observations of superconductivity are supported and even predicted by the BCS electron-phonon theory of superconductivity [14].

In the Van der Pauw four probe resistance measurements, two electrodes are used to supply the current I at two positions on the boundary of the sample, and another two electrodes at other positions on the boundary of the sample are used to measure a voltage difference V, from which the resistance $R = V/I$ is obtained. By alternating the current and voltage electrodes, the resistivity of a *two-dimensional homogeneous sample* can be extracted, according to the famous Van der Pauw formula. For the particular situation where the alternative positions of the electrodes is symmetric, the following formula results for the resistivity:

$$\rho = \frac{\pi}{ln2} dR \qquad (1)$$

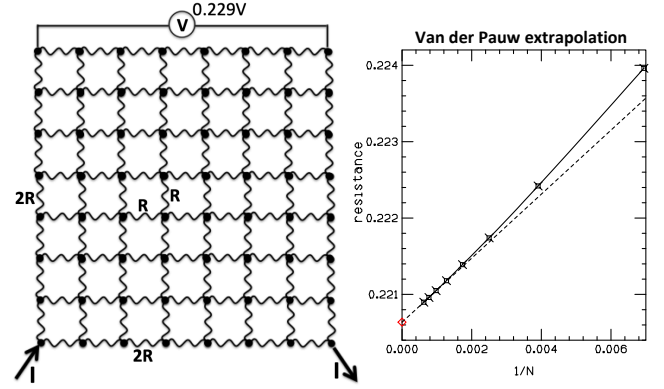where R is the measured resistance V/I and d is the

FIG. 1: Left panel: two-dimensional grid of resistors to model a two-dimensional continuous sample. The lattice has N=nxn sites, with n=8. Resistors are $R = 1\Omega$. The voltage difference between the top left and right corners is 0.229V when a current $I = 1A$ is injected at the bottom left corner and extracted at the bottom right corner. The right panel shows the corresponding voltage results for larger N, that converge to the Van der Pauw limit $ln2/\pi = 0.22064$ for $N \to \infty$.

thickness of the sample. In the DAC experiments, resistance is usually reported using only one positioning of the electrodes. In the rare cases where alternate positionings of electrodes are reported [4, 8] the results show different magnitudes and temperature dependence, clearly indicating sample inhomogeneity.

In this paper I point out that what is interpreted as resistance in these measurements has a more complicated relation with the resistance of the sample than is usually assumed, and in particular that the very small values measured do not necessarily indicate that the material is becoming more superconducting, nor even more conducting.

I use a two-dimensional square grid of resistors [15] to model the samples in the DAC's, as shown in Fig. 1 left panel. The current (voltage) electrodes are at the bottom (top). The resistors in the interior have half the value of the resistors at the edges, since when superposing the square elements the interior resistances are halved [15]. In the limit of a large lattice, the voltage measured converges to the Van der Pauw result given in Eq. (1),
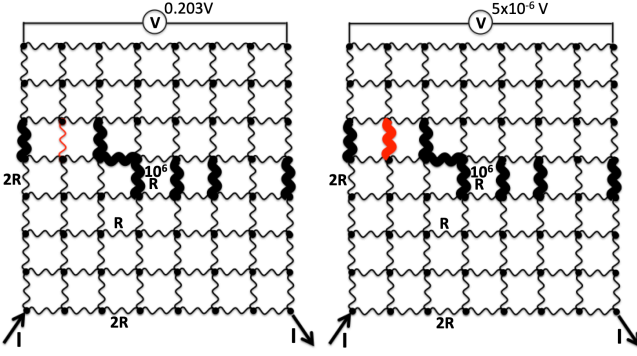
FIG. 2: Two examples of inhomogeneous samples, differing in the value of one resistor (shown in red). The thin resistors have value $R = 1\Omega$, the thick resistors have value $10^6\Omega$. For the configuration shown on the right panel, the 'resistance' inferred from the measured voltage is a factor 2.5×10^{-5} ($= 5 \times 10^{-6}/0.203$) smaller than the one on the left panel.

as shown on the right panel of Fig. 1.

The experiments with hydrides under high pressure in DAC's use an analogous geometry. When the voltage measured as a function of temperature drops even slightly when the temperature is lowered, it is interpreted as a drop in resistance signaling the 'onset' of superconductivity [16]. When the measured voltage drops to very small values it is interpreted as proof of superconductivity [1, 3]. More often than not, the procedure used is warming rather than cooling, so the resistance increases from very small values to finite values as the temperature increases.

Fig. 2 shows two examples of inhomogeneous samples for our model, differing in the value of one resistor. The thick resistors have value 10^6 times larger than the thin resistors. If, when cooling the material represented by the left panel, the resistance value of the one resistor shown in red on the left panel *increases* from 1Ω to $10^6\Omega$, the measured voltage will *decrease* from $0.203V$ to $5 \times 10^{-6}V$. For those expecting to find superconductivity, the measured decrease in voltage by 5 orders of magnitude would be interpreted as clear evidence of superconductivity and not by what actually is happening in this sample, namely an increase in the value of one resistor.

Why is there such a large change in voltage between the left and right panels of Fig. 2? The reason is, on the right panel the lower and upper parts of the sample are effectively disconnected from each other, since there is one single path where current can flow from the lower to the upper part, however there is no return path for the current. As a consequence, essentially no current flows in the upper half of the sample, and a negligible voltage difference between the voltage electrodes results. Instead, on the left panel there is a path for current to flow upward on the left side (through the red resistor) and downward on the right side, and as a consequence current flows in the upper part of the sample and an appreciable voltage
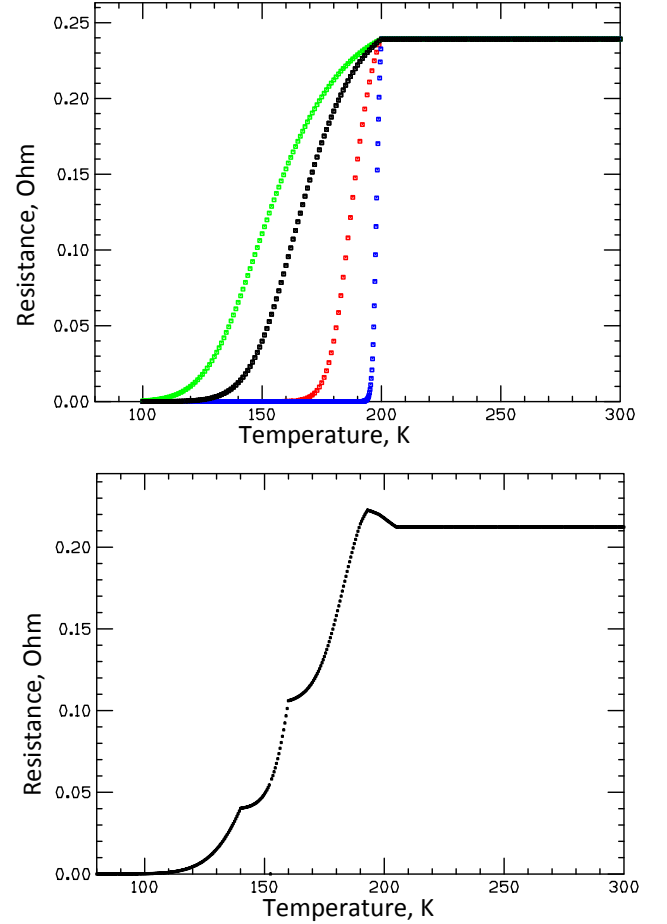

FIG. 3: Top panel: temperature dependence of the measured voltage for the circuit of the right panel of Fig. 2, with the thick resistors all having the same value given by Eq. (3) with $\Delta = 0.16eV, 0.24eV, 0.71eV, 4.5eV$ for the green, black, red and blue points respectively. Bottom panel: an example of behavior found when different resistors have different Δ values.

difference between the voltage electrodes results. Note also that if one were to connect a current source between an electrode on the bottom row and one on the top row to check for connectivity of the samples a current will flow for both samples, and the fact that for the sample on the right panel the upper and lower parts are effectively disconnected for the voltage measurement would not be detected.

The temperature dependence of the resistance of hydrides samples at temperatures above the purported superconducting transitions is sometimes found to be metallic-like (decreasing with decreasing temperature) and sometimes semiconducting-like (increasing with decreasing temperature) [12]. This suggests that there are both metallic and semiconducting regions in these inhomogeneous samples, with one or the other dominating. Assuming that the thick resistors shown in Fig. 2 are parts of the sample with semiconducting behavior, their
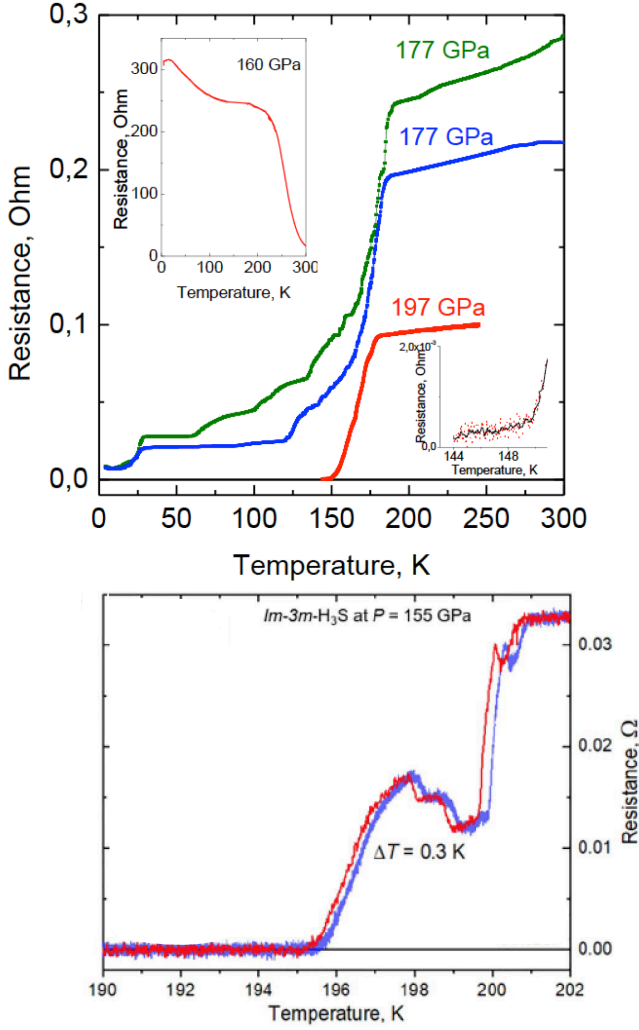
FIG. 4: Top panel: Figure 3 of the Supplementary information in the paper where high temperature superconductivity in sulfur hydride was first reported, Ref. [2]. Bottom panel: Figure 1e of Ref. [4], showing typical resistance measurements for sulfur hydride 8 years later. The figure caption of the top panel reads in full [2]: *"Transformation of the superconducting state in the H_2S sample with pressure, temperature and time. At pressures up to 155 GPa there is only one SC step at $\sim 60K$. After warming to 300 K at this pressure the resistance dropped to $\sim 5\Omega$ and then below 1Ω at pressurizing to 177 GPa. The step at $\sim 180K$ developed at the cooling (olive line). It became more pronounced (blue line) with time (15 hours). After pressurizing to 197 GPa at 300 K and next cooling the minimum resistance reached $R = 1.7 \times 10^{-4}\Omega$ at 144 K (inset). Corresponding resistivity $\rho \sim 1.7 \times 10^{-10}\Omega$ m ~ 50 times lower than for copper (at 150 K $\rho = 70 \times 10^{-10}\Omega$ m, Ref. 27). There are notable oscillations on the R(T) pronounced at the olive curve. We observed these oscillations with period of 25-30 K in a number of runs. The resistance plots (olive and blue lines) taken in PPMS were averaged from the measurements with increasing and decreasing of temperature. The rest of the plots are measurements in optical cryostat at slow (about 5 hours) warming so the temperature was close to equilibrium."*

temperature dependence can be expected to be of the form

$$R \sim R_0 e^{\Delta/(k_B T)}. \qquad (2)$$

In Fig. 3 top panel we show the resulting temperature dependence of voltage and hence "resistance" V/I for different Δ values assuming all the thick resistors in Fig. 2 right panel are governed by the same Δ. Depending on the value of Δ, a more or less sharp "superconducting transition" apparently takes place. The widths of superconducting transitions reported for these materials vary very widely, in one extreme case it varies by a factor of 1000 for different samples of the same material prepared under identical conditions [13]. That is clearly inconsistent with the assumption that the transition originates in superconductivity [17].

If instead we use different Δ's for different resistors, we can obtain behavior such as shown in Fig. 3 bottom panel. It displays oscillations of the resistance with temperature, as well as a region where the resistance increases when T is lowered. Such behaviors are commonly seen in hydride resistance measurements. Note that all of the temperature dependence in Fig. 3 arises from an *increase* in resistance values as temperature decreases rather than the opposite. By assuming semiconducting behavior for some of the resistors in Fig. 2 and metallic behavior for others a wide variety of temperature dependence of voltage with temperature will result.

Thus I propose, as an alternative explanation to the assumed superconductivity of hydrides under high pressure, evidenced by measurements such as the ones shown in Fig. 4, that measured small or vanishing voltages may not originate in small or vanishing resistivity but instead in the fact that the part of the sample where the voltage electrodes reside becomes effectively disconnected from the part where the current electrodes reside and electric current flows, due to changes in the resistivity and spatial distribution of different parts of very inhomogeneous samples as function of temperature and pressure. When the temperature changes, the DAC's will undergo contraction and expansion, pressure gradients will develop and change, and subregions of the sample with different hydrogen contents may undergo large changes in intrinsic resistance and connectivity and transition between metallic and semiconducting behavior. The example shown in Fig. 2 is extreme, to demonstrate the principle involved, but indicates that a large variety of behaviors may be expected in such inhomogeneous samples, that would cause the measurements not to reflect what at first sight one would assume they reflect, i.e. a decrease (increase) in resistivity when the measured voltage decreases (increases).

The measurements shown in Fig. 4 and its extensive figure caption supports the plausibility of the scenario proposed here. The measured voltage, interpreted as reflecting the resistance of the sample, depends on the history of the measurement, first decreasing as the temperature increases, then decreasing as the temperature

decreases, also changing as a function of time with no changes in external variables. These features indicate that random rearrangement in the configuration of different parts of the sample are taking place, with associated changes in the local resistivity. The steps (oscillations) that are seen particularly in the green curve in Fig. 4 top panel and discussed in the figure caption are widely seen in these types of measurements. Rather than originating in multiple superconducting transitions they could simply arise from connection and disconnection of conducting pathways such as in the example shown in Fig. 3 bottom panel. Note that in the green and blue curves shown in the upper panel of Fig. 4, nothing close to zero resistance is reached. Only the red curve in that figure shows a very small resistance, claimed to originate in a resistivity two orders of magnitude smaller than that of pure copper [3]. However that inference assumes that the sample is homogenous, Instead, with an inhomogeneous sample reflecting the physics of Fig. 2 right panel, even much smaller 'resistivity' could be inferred that does not reflect the actual resistivity of the sample.

It is also interesting to note the discussion in Ref. [4] with respect to the behavior shown in the bottom panel. of Fig. 4, which we reproduce here: *"The interpretation in terms of the emergence of superconductivity when the $R(T)$ dependence sharply drops to zero below Tc is obvious for perfect samples. However, many real samples are contaminated by unreacted precursor compounds, contain impurity by-product phases (e.g., unsaturated lower hydrides), or are poorly crystallized. These imperfections are often unavoidable, since some tiny areas of a sample are not thoroughly heated in order to prevent the electrical leads from damage by a pulsed laser. In addition, samples of a larger size, which are not surrounded by a quasi-hydrostatic medium (e.g., excess hydrogen), have considerable pressure gradients. In such samples, the superconducting transition broadens and displays additional steps, indicating that the $R(T)$ dependence is affected by non-uniform current flow (Fig. 2c-e). These distortions of the superconducting transition were also observed in other superconductors [42]... Perhaps even more complicated is another kind of distortions of the superconducting transition: a peak in R(T) [43–45] — an anomalous increase of the resistance that precedes the sharp drop to zero...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"*.

Thus, while the authors of Ref. [4] conclude that the wide variety of anomalous behavior observed is not only not inconsistent with superconductivity but *"strongly supports superconductivity"*, I argue that that it is instead strong evidence in support of the scenario proposed here that does not involve superconductivity.

Resistance measurements for these materials are quite generally widely variable from experiment to experiment.
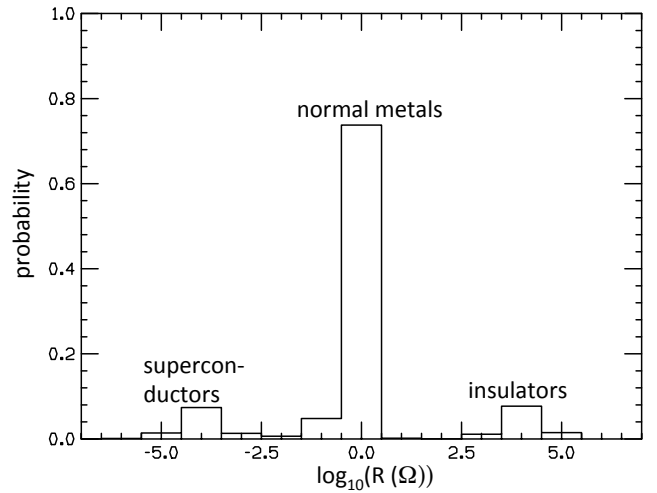

FIG. 5: For an 8x8 lattice of resistors with resistance 1Ω with probability 0.6 and $10^6\Omega$ with probability 0.4 randomly arranged, the histogram shows the probability of measuring various resistance values by measuring the voltage difference between the electrodes at the top as shown in Fig. 2.

Note that the blue and red curves in Fig. 4 top panel for pressure 177 GPa don't show small resistance even at temperatures well below 20K. Still, in Ref. [3] Fig. 1 right panel it is reported that the critical temperature of sulfur hydride at 177 GPa is around 75K, and in the same Ref. [3] Fig. 2 right panel it is reported that the critical temperature of sulfur hydride at 177 GPa is around 180K. Measurements on sulfur hydride performed several years after the initial discovery have been reported to show no vanishing resistance at any temperature [8, 18]. In the process of laser heating the precursor sample with a few micron wide laser spot size rastering over the material, the way these samples are usually made, it is to be expected that multiple phases and residual precursors remain, giving rise to inhomogeneous samples with regions of widely varying resistivity, with different spatial distribution each time a new sample is processed. Rearrangements will also occur in the processes of compression and decompression, heating and cooling, as evidenced by hysteresis often reported for these measurements. Variable hydrogen content in various parts of the samples together with the pressure gradients is likely to result in a complicated morphology involving coexisting metallic and semiconducting regions as well as voids, severely affecting the electrical connectivity.

In particular, reference [13] reports that only one third of nitrogen-doped lutetium hydride samples manufactured by the same protocol are superconducting (at room temperature). This clearly indicates that each time a sample is made in that laboratory a different configuration results, that can radically change its behavior. If two thirds of the time the resulting sample has the connectivity shown on the left panel of Fig. 2, and one third of the time the one shown on the right panel of Fig. 2,
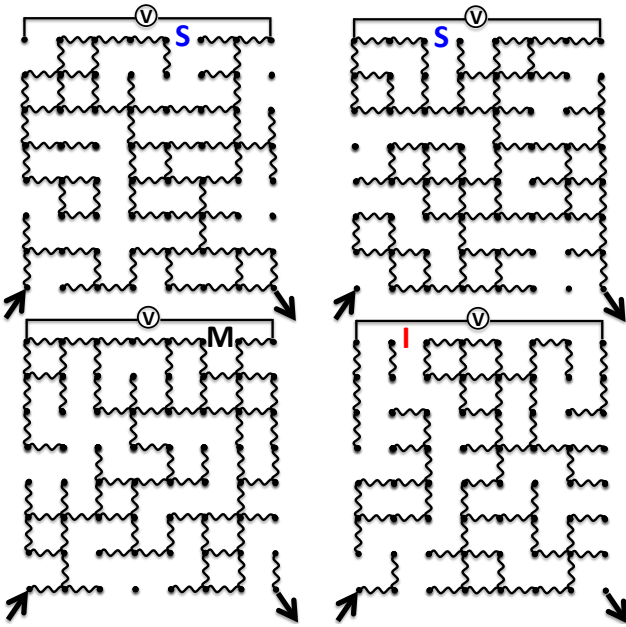
FIG. 6: Examples of configurations giving rise to 'superconducting' (S), 'metallic' (M) and 'insulating' (I) behavior in the histogram of Fig. 5. The resistors shown have value 1Ω, the absence of resistor between two nodes means a resistor with value $10^6\Omega$ between those nodes. The resistances obtained by measuring the voltage between the upper left and right corners are $4.23 \times 10^{-5}\Omega$ for the upper left panel (S), $1.08 \times 10^{-5}\Omega$ for the upper right panel (S), 0.55Ω for the lower left panel (M) and $58,891\Omega$ for the lower right panel (I). The order of magnitude of these resistances is easily understood by examination of the topology of the panels.

the rate of 'success' in the sample manufacturing of Ref. [13] is simply explained, not by superconductivity but instead by topology.

In our computer laboratory we have not yet been able to achieve the success rate reported in Ref. [13]. Instead, Fig. 5 shows what we obtained by randomly distributing resistors on an 8x8 resistor array with values 1Ω. with probability 0.6 and $10^6\Omega$ with probability 0.4. It can be seen that most samples fabricated in that way are 'normal

metals', with resistance of order 1Ω, approximately 10% are 'insulators', with resistance of order $10^4\Omega$, and approximately 10% are 'superconductors', with resistance of order $10^{-4}\Omega$. Clearly, the wide variation in resistance values results from the different connectivities of the samples. Fig. 6 illustrates examples of configurations giving rise to the different behaviors.

It is likely to be also the case that often measurements performed on 'bad samples' are not reported by the authors. It is natural that authors will be inclined to present in their papers mainly measurements of their samples that as the temperature is lowered acquire topology such as shown in the upper two panels of Fig. 6, that are consistent with the interpretation of superconductivity, and not include in their papers measurements of other samples behaving as the ones on the lower panels of Fig. 6, that would not be consistent with superconductivity. Confirmation bias of authors, expert reviewers, and high profile journal editors, all acolytes of BCS-electron-phonon theory, is likely to play an important role in this process.

In this paper we have not addressed the issue of magnetic field dependence of resistance. It is widely reported that observed resistance drops in hydrides shift to lower temperatures upon application of large magnetic fields, and this is interpreted as evidence of superconducting behavior with large values of the upper critical field. Clearly, a different interpretation is required if no superconductivity is involved. I note that giant magnetoresistance has been reported for inhomogeneous semiconducting samples due to geometric effects [19], as well as for semiconductor-metal composites in the van der Pauw geometry [20, 21]. This clearly suggests an alternative explanation for the observed magnetoresistance within the scenario proposed here which will be explored in future work.

Acknowledgments

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