Meissner effect in nonstandard superconductors

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It was recently pointed out that so-called “superhydrides”, hydrogen-rich materials that appear to become superconducting at high temperatures and pressures, exhibit physical properties that are different from both conventional and unconventional standard type I and type II superconductors [1, 2]. Here we consider magnetic field expulsion in the first material in this class discovered in 2015, sulfur hydride [3]. A nuclear resonant scattering experiment has been interpreted as demonstration that the Meissner effect takes place in this material [4, 5]. Here we point out that the observed effect, under the assumption that the system is in thermodynamic equilibrium, implies a Meissner pressure [6] in this material that is much larger than that of standard superconductors. This suggests that hydride superconductors are qualitatively different from the known standard superconductors if they are superconductors.

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I. INTRODUCTION

The 2015 discovery of high temperature superconductivity in pressurized sulfur hydride \([3] (H_2S)\) with critical temperature up to 203 K was the first of several metal hydrides recently reported to be superconducting at high temperatures and pressures between 100 GPa and 250 GPa. These include phosphorous hydride at above 100 K [8], lanthanum hydride at 250 K [9], above 260 K [10] and above 550 K [11], yttrium hydride at 243 K [12–14], thorium hydride at 161 K [15], lanthanum-yttrium ternary hydrides at 253 K [16], carbonaceous sulfur hydride at room temperature [17] and cerium hydride above 110 K [18]. For all these materials, resistance versus temperature curves exhibit sharp drops at temperatures that have been interpreted as superconducting transition temperatures, and application of large magnetic fields shifts these transition temperatures to lower values. These materials have been characterized as strongly type II superconductors, with upper critical fields in the range 60–150 T [19].

However, in recent work we [1] and others [2] have argued that features of the resistive transition in a magnetic field appear to be in conflict with the behavior seen in standard superconductors, explained by the conventional theory of superconductivity [20], and hence that these materials, if they are superconductors, are ‘nonstandard superconductors’ [1].

To establish that superconductivity exists in these materials it would be important to show that they expel magnetic fields, i.e. the Meissner effect; alternatively even if somewhat less compelling, that they do not allow penetration of magnetic fields, i.e. magnetic field exclusion. In Refs. [4, 5], it has been claimed that magnetic field exclusion in sulfur hydride has been detected through a novel nuclear resonance scattering experiment. However, here we show that a standard superconductor, whether conventional or unconventional, would not show this behavior in thermodynamic equilibrium. We conclude that, under this assumption, this observation provides further evidence that sulfur hydride, and by inference other hydride superconductors, are either nonstandard superconductors [1], or they are not superconductors. In a separate paper [21] we consider the possibility that the measurements reported in ref. [4] did not reflect the state of the superconductor in thermodynamic equilibrium.

II. THE NRS EXPERIMENT

In Ref. [4], a 2.6 – \(\mu\)m thick foil of tin was immersed into the \(H_2S\) specimen [22]. The tin was enriched to 95% with the \(^{119}\text{Sn}\) isotope to serve as the sensor. The sensor monitors the magnetic field via the magnetic interaction at the \(^{119}\text{Sn}\) nucleus as detected by nuclear resonant scattering (NRS) of synchrotron radiation. The presence of magnetic field at tin nuclei was identified by quantum beats in the time spectra of NRS [23].

As a control, the measurements were conducted simultaneously with two diamond anvil cells (DACs). One contained the \(H_2S\) sample, the other contained only \(H_2\). Both had identical \(^{119}\text{Sn}\)-enriched foils, and were in the same applied magnetic field and temperature. It was found that the spectra measured were similar for both samples above 100 K, but differed markedly for temperatures below 50 K. While the control sample response was consistent with having a magnetic field in its interior equal to the applied magnetic field, \(H_{\text{ext}} \sim 0.68\) T, the response of the \(H_2S\) sample indicated that the magnetic field in the interior of the sample dropped to zero for temperatures 50 K and below when the magnetic field was applied perpendicular to the sample, and to about a third of the applied field when the magnetic field was applied parallel to the sample.

The experiment did not attempt to detect the Meissner effect, i.e. magnetic field expulsion, as the paper states, but rather magnetic field exclusion [7]. The sample was first cooled in the absence of a magnetic field and subsequently the magnetic field was applied. The authors concluded that the experiment showed that the magnetic
field was excluded from the interior of the sample at low temperatures due to the Meissner effect, and therefore the sample had to be in the superconducting state at low temperatures.

In the following sections we show that a standard superconductor in thermodynamic equilibrium would not have excluded the magnetic field in the conditions of the experiment.

III. MAGNETIC FIELD EXCLUSION

Let us first consider the geometry where the applied magnetic field is perpendicular to the Sn foil, because it is in this geometry where the largest deviation from the expected behavior of standard superconductors occurs.

Figure 1 shows the geometry, also shown in Figure S6 of Ref. [4]. The external magnetic field had magnitude $H_{\text{ext}} = 0.68$ T. The figure shows the assumed exclusion of the magnetic field from the sample interior. It is immediately obvious that the magnetic field at the edges of the sample is much larger than the applied field, due to demagnetization. For a cylindrical geometry with aspect ratio height/radius = 0.333, as shown in Fig. 1, the demagnetizing factor is approximately $N_z \approx 0.727$ [24]. This indicates that the magnetic field at the edges of the sample is a factor $1/(1 - N_z) = 3.7$ times larger than the applied field. So the magnetic field at the edge of the sample is

$$H_{\text{edge}} = 2.5 \text{ T.}$$

If this is a type I superconductor, it would imply that the thermodynamic critical field $H_c$ is larger than 2.5 T. This would be unprecedented. The largest known critical fields for standard type I superconductors are of order 0.05 T, i.e. 50 times smaller. If this is a type II superconductor in thermodynamic equilibrium, it would imply that the lower critical field $H_{c1}$ is larger than 2.5 T. This would be even more unprecedented, since $H_{c1} < H_c$ within the standard theory of superconductivity.

In Ref. [3], the upper critical field $H_{c2}$ was estimated to be between 60 and 80 T. Let us assume $H_{c2} = 68$ T, corresponding to a zero temperature coherence length $\xi = 2.20$ nm. From magnetization measurements, it was concluded in Ref. [3] that the lower critical field is approximately $H_{c1} \sim 0.03$ T. The applied field is then 1/100 of $H_{c2}$ and much larger than $H_{c1}$. From this, the London penetration depth was estimated to be $\lambda_L = 125$ nm [3]. Alternatively, Talantsev estimated a value $\lambda_L = 189$ nm from self-field critical current data [25]. We will use the value of $\lambda_L$ of Ref. [3] for definiteness; note that our conclusions would not change using a larger $\lambda_L$ value.

It is clear that if this was a standard superconductor that will reach its thermodynamic equilibrium state, the applied field which is much larger than $H_{c1}$ would penetrate throughout the superconductor, no matter what the geometry, in particular in the two configurations used in [4], magnetic field perpendicular to the Sn foil (Fig.1) and parallel to it. For a sample of cross-sectional area $A$ perpendicular to the magnetic field, the number of vortices $N_v$ is determined by the equation

$$H_{\text{ext}} A = N_v \phi_0. \quad (2)$$

The upper critical field is given by

$$H_{c2} = \frac{\phi_0}{2\pi\xi^2} \quad (3)$$

so the area per vortex is

$$a_v = \frac{A}{N_v} = 2\pi\xi^2 \frac{H_{c2}}{H_{\text{ext}}} \quad (4)$$

so for $H_{\text{ext}}/H_{c2} = 0.01$,

$$a_v = \pi(\sqrt{200}\xi)^2 \quad (5)$$

so the distance between vortex cores is approximately

$$d_v = 2\sqrt{200}\xi = 62 \text{ nm}, \quad (6)$$

which is half the estimated London penetration depth. This indicates that the magnetic field is nearly uniform in the mixed state of this superconductor, with magnitude in the range

$$e^{d_v/(2\lambda_L)} H_{\text{ext}} < H < H_{\text{ext}} \quad (7)$$

or

$$0.78 H_{\text{ext}} < H < H_{\text{ext}}. \quad (8)$$

So using the parameters for this superconductor inferred by the authors of Ref. [3] and assuming standard superconductivity, we conclude that in both geometries used in Ref. [4], applied magnetic field perpendicular and parallel to the Sn film, the magnetic field would be uniform or nearly uniform inside the sample and inside the Sn film when the sample is in the superconducting state.
in thermodynamic equilibrium. However this is inconsistent with the experimental results presented in Fig. 4 of Ref. [4], that indicate that the magnetic field drops to zero in one geometry and to one third of the applied value in the other geometry, for temperatures below 50 K, as is shown in Fig. 2.

But let us assume that for some unknown reason the magnetic field is indeed zero in the interior of the sample, as claimed by the authors of ref. [4]. What would be the current necessary so that the field does not penetrate? A lower bound to that current would be a current circulating near the surface that generates a magnetic field $H_{\text{edge}} = 0.68$ T at the center of the sample. For a circular loop of current of radius $a$ with current $I$ circulating, the magnetic field at the center is

$$B = \frac{2\pi I}{ca}$$

which for $B = 0.68$ T and $a = 15\ \mu m$ as shown in Fig. 1 yields $I = 16$ Amp. Assuming the current circulates within the London penetration depth $\lambda_L = 125$ nm of the surface and sample thickness 5 $\mu m$ as shown in Fig. 1 yields for the current density

$$J = 2.6 \times 10^9 \frac{\text{Amp}}{\text{cm}^2}.$$  

Therefore, the critical current density would have to be larger than the value Eq. (10). Critical current densities for all known standard superconductors are about 2 orders of magnitude lower than that value. This then suggests that if $H_3S$ is a superconductor, it is a nonstandard superconductor, as defined in Ref. [1]. Note that we also found in Ref. [1], based on analysis of the resistive transition in a magnetic field, that the critical current densities of nonstandard superconductors are much higher than those of standard superconductors.

IV. NONSTANDARD SUPERCONDUCTIVITY IN $H_3S$

To further explore the possibility that if $H_3S$ is a superconductor it is a nonstandard superconductor, let us ignore the values of $\lambda_L$ reported in Refs. [3, 25] mentioned above and instead infer its value using the standard theory of superconductivity. As discussed in the previous section, the total magnetic field at the edge of the sample would be 2.5 T if the field doesn’t penetrate. Within the standard theory of superconductivity this implies that the lower critical field $H_{c1}$ is larger than 2.5 T even at temperatures around 100 K where the magnetic field starts to be excluded. Let us explore the implications of this. For simplicity we will assume $H_{c1} = 2.5$ T at $T = 0$, although in reality it would have to be even larger if it is 2.5 T at $\sim 100$ K.

Using the expression for the lower critical field [20, 26]

$$H_{c1}(0) = \frac{\phi_0}{4\pi \lambda_L(0)^2} \ln \left( \frac{\lambda_L(0)}{\xi(0)} \right)$$

we have for the London penetration depth at zero temperature

$$\lambda_L(0) = \xi(0) \sqrt{\frac{H_{c2}(0)}{2H_{c1}(0)}} \ln \left( \frac{\lambda_L(0)}{\xi(0)} \right)$$

and with $H_{c2}(0) = 68$ T, $H_{c1}(0) = 2.5$ T

$$\lambda_L(0) = 3.69 \sqrt{\ln \left( \frac{\lambda_L(0)}{\xi(0)} \right)}$$

and we obtain $\lambda_L(0) = 4.54 \xi(0) = 10.0$ nm. So the material would have to be a weakly type II superconductor, with $\kappa = \lambda_L(0)/\xi(0) = 4.5$, to exclude the applied magnetic field as found in the NRS experiment, instead of $\kappa > 50$ as inferred in Refs. [3, 25]. In facy, it was argued in Ref. [17] that a similar material in this class, CSH, may be such a weakly type II superconductor, with $\kappa$ as low as 1.7 [27].

However, this would be contrary to all expectations for this material (and for CSH [1]) based on the standard theory of superconductivity [3, 19, 25]. In addition, it would imply that the thermodynamic critical field, given by

$$H_c(T) = \frac{\phi_0}{2\sqrt{2}\pi \lambda_L(T)\xi(T)}$$

has the value

$$H_c(0) = 10.6$$

which is more than an order of magnitude larger than is found for any standard superconductor, and implies an enormous condensation energy. This in turn exerts an enormous ‘Meissner pressure’ $H_c^2/(8\pi)$ [6] which is
necessary to account for the experimental results seen in Fig. 2 in the configuration of Fig. 1.

Within the standard theory of superconductivity the thermodynamic critical field obeys the relation

$$\frac{H_c^2(0)}{8\pi} = \frac{1}{2} g(\epsilon_F) \Delta^2(0)$$  \hspace{1cm} (16)$$

where $\Delta(0)$ is the energy gap at zero temperature and $g(\epsilon_F)$ is the density of states per spin at the Fermi energy. So we would have to assume that this relation which holds for standard superconductors fails for the superhydrides for unknown reasons. Alternatively, this value of $H_c(0)$ would imply that either the density of states or the energy gap is much larger than in standard superconductors. Assuming the standard BCS relation between energy gap and critical temperature, the density of states that would be implied by the value Eq. (16) for the critical field is

$$g(\epsilon_F) = \frac{0.586 \text{ states}}{\text{spin} - eV\text{A}^3}. \hspace{1cm} (17)$$

This is an enormous density of states. For comparison, using the standard theory the density of states of sulfur hydride was estimated to be 0.019 states/(spin$-eV$/A$^3$) [19], 30 times smaller.

Assuming the density of states is given by the free electron expression with effective mass $m^*$ we have

$$g(\epsilon_F) = \frac{0.0206}{\text{spin} - eV\text{A}^2} \frac{m^*}{m_e} n^{1/3} \hspace{1cm} (18)$$

with $n$ the number density. For the density of states given by Eq. (17) this yields for the Wigner Seitz radius

$$r_s = 0.022\frac{m^*}{m_e} \text{Å}. \hspace{1cm} (19)$$

The $H - H$ distance in sulfur hydride at pressures above 150 GPa is approximately 1.4 Å. Assuming $r_s = 0.7$ Å yields

$$\frac{m^*}{m} \approx 32. \hspace{1cm} (20)$$

However, the effective mass enhancement resulting from the electron-phonon interaction is expected to be only around a factor of 3. The theoretical calculations that claim to explain the observed values of $T_c$ in $H_3S$ [28–34] are not compatible with an effective mass enhancement as given by Eq. (20).

Note also that if the London penetration depth is $\lambda_L \sim 10.0$ nm, as given by this analysis rather than 125 nm, the critical current would have to be larger than $3.2 \times 10^{10}$ Amp/cm$^2$, even more anomalous than the value given by Eq. (10).

We conclude that if the experimental results reported in Ref. [4] reflect the properties of $H_3S$ in thermodynamic equilibrium, $H_3S$ cannot be explained by the standard theory of superconductivity. In that case, $H_3S$ would be a novel nonstandard superconductor that excludes magnetic fields that are two orders of magnitude larger than what the standard theory predicts it can exclude. Presumably this is would be true for all the other nonstandard superconductors [1], i.e. all other hydrogen-rich materials that superconduct at high temperatures under high pressures.

V. DISCUSSION

If sulfur hydride in thermodynamic equilibrium truly excludes magnetic fields of the magnitude claimed in the geometries used in this experiment, it would imply that its superconductivity is very nonstandard. It would have a “Meissner effect on steroids”. This new property of nonstandard superconductors would be consistent with what was found in Ref. [1], that nonstandard superconductors should have critical currents that are orders of magnitude higher than those of standard superconductors. A new theory of the electrodynamics of these materials would be required to describe their very unusual properties. These properties would lend them very useful for practical applications such as levitating trains.

However, if these materials were so different from standard superconductors we also have to ask: why would it be that standard BCS-Eliashberg theory appears to be able to accurately predict their transition temperatures as claimed in the literature [28–40]? We suggest that ‘superflexibility’ [41] may have something to do with it, whether or not these materials are superconductors.

There is also the possibility that the experiment reported in Ref. [4] is flawed for some reason. If so, it would not provide supporting evidence to the claim that sulfur hydride under pressure is a high temperature superconductor [3, 19], contrary to what is generally assumed [42]. This would cast further doubt on the claim that superhydrides are high temperature superconductors, adding to the arguments given in [1, 2, 43].

We will consider the alternative possibility that the measurements in [4] do not reflect the properties of $H_3S$ in thermodynamic equilibrium, and its implications, in a separate paper [21].

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