Observation of wetting-like phase transitions in a surface-enhanced type-I superconductor

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Abstract. Superconductivity in single crystal Sn samples with surface-enhanced order parameter is studied experimentally. Controllable surface enhancement is achieved by mechanical polishing or by ion irradiation. A first-order surface superconductivity transition is found in parallel magnetic fields close to the bulk critical field \(H_{c3}(T)\) and for temperatures above 0.8\(T_c\) up till a surface critical temperature \(T_{cs} > T_c\), where \(T_c\) is the bulk critical temperature. The resulting phase diagram agrees with that predicted for interfacedelocalization or wetting transitions in type-I superconductors, based on the Ginzburg–Landau theory.

In this paper, we address the following fundamental issues. What is the nature of surface superconductivity? Is it possible that the superconducting phase ‘wets’ the specimen surface, meaning that a macroscopic superconducting sheath intrudes between the surface and the normal phase? Can the interface delocalization or ‘wetting’ phase diagram, predicted for surface-enhanced type-I superconductors, be verified experimentally? If so, what is the character of the phase transitions involved? How can surface enhancement of superconductivity be achieved in a controlled and systematic way?

Surface superconductivity has continued to intrigue experimentalists and theorists alike since its prediction in 1963 [1]. Continuous nucleation of superconductivity occurs at the sample surface below a parallel magnetic field known as \(H_{c3}(T)\), with \(T < T_c\), provided the Ginzburg–Landau (GL) parameter \(\kappa\) exceeds 0.41. This effect arises for surfaces in contact with vacuum or
an insulator. For materials with $\kappa < 0.41$, $H_{c3}$ lies below the bulk critical field $H_c$. Then there is no stable surface superconductivity above $H_c$ and, decreasing $H$ below $H_c$, $H_{c3}$ is the metastability limit of the normal state.

A surprising transformation of surface superconductivity, in which the superconducting surface sheath can develop ‘bulk’ proportions, was predicted in 1995 for different surfaces, endowed with enhancement of the superconducting order parameter [2]. In this interface delocalization or ‘wetting’ scenario the sheath thickness becomes macroscopic when $H$ is lowered to $H_c$ for temperatures above a ‘wetting’ temperature $T_w$. Further, surface superconductivity extends to a surface critical temperature $T_{cs} > T_c$. This equilibrium phenomenon is very different from fluctuation conductivity [3]. The phase diagram for $\kappa < 0.374$ features a first-order surface ‘prewetting’ transition from the normal state to a superconducting surface sheath, for $T_w < T < T_{cs}$. For $0.374 < \kappa < 0.707$ the predicted wetting transition is critical instead of first order [2]. For mesoscopic samples the theory predicts a significant increase of $T_c$ [4] on the basis of which new applications can be expected.

The similarity between ‘wetting’ phenomena in type-I superconductors and those in fluids or Ising magnets ([5, 6]; for a recent review, see [7]) comes from the fact that there is a positive excess free energy $\gamma_0$ associated with the interface between the coexisting bulk phases, in our case the normal phase and the superconducting Meissner phase. In addition, there is preferential adsorption of one bulk phase at the surface, in our case the superconducting phase. For $\kappa > 0.41$ and surfaces in contact with an insulator this leads to nucleation at $H_{c3}(T)$ but this is not quite sufficient to induce wetting. Complete wetting is possible only if the difference of surface free energies of normal and superconducting phases, $\gamma_n - \gamma_s$, is large enough to match the interfacial tension $\gamma_0$. This requires other surfaces, with enhancement of the order parameter, i.e., negative surface extrapolation length $b$ in the GL theory [2].

Phase transitions from partial to complete wetting have been observed in various liquid–liquid and liquid–gas systems in a broad temperature range, from cryogenic (see, e.g., [8]) to thousands of degrees [9]. However, in spite of continuing interest in the phenomenon [10], no experimental study has yet been dedicated to verify the theory of interface delocalization transitions in superconductors. Note that the so-called ‘twinning-plane superconductivity’ in Sn [11], which was a posteriori interpreted as prewetting [2, 12], originates from internal defects. These cannot be manipulated systematically, and certainly not reversibly, in contrast with the outer surface of the sample [13].

Pure Sn is a classical type-I superconductor with $\kappa \approx 0.15$ [14]. $T_c$ as measured by us is $3.73 \pm 0.005$ K, consistent with previous work [15]. As was recently shown [13], mechanical polishing (surface cold working) induces reversible surface enhancement of the order parameter in single crystal Sn samples. Enhancement of superconductivity by surface cold working was demonstrated long ago on an InBi alloy [16]. Possible origins of this effect in Sn are discussed in [13]. One of the samples we use is a polished single crystal Sn sample described in [13] (sample no. 2), below referred to as ‘polished’. Another single crystal sample from the same supplier (Alfa Aesar) has the same shape (spark cut disk, 7 mm diameter and 1 mm thickness) and purity (99.9999%) as the polished sample. We refer to it as ‘plain’. Its quality was checked by measuring dc magnetization at supercritical temperatures 3.74 and 3.76 K, yielding the same diamagnetic response as for the annealed samples described in [13], which is an order of magnitude lower than for the polished sample. Upon completing a full set of measurements, one side of the plain sample was modified via irradiation with Xe ions (using the Leuven ion separator), and hence is referred to as ‘implanted’.
Irradiation with noble gas ions can be viewed as precision surface cold working, by far more controllable and uniform than polishing. If so, ion irradiation should induce enhanced surface superconductivity. Indeed, irradiation by Xe$^{++}$ ions with energy 160 keV and a fluence of $10^{16}$ cm$^{-2}$ yielded an increase in supercritical diamagnetic response of about 50% with respect to the magnetization in the plain sample. Consecutive irradiation with a ten times larger fluence of 80 keV Xe$^+$ ions resulted in an enhancement of supercritical diamagnetism by a factor of 5. This is about half of the surface diamagnetism of the polished sample (see figure 1). Taking into account that polishing was applied to both sides [13], this means that the implanted and polished samples possess approximately the same effective surface enhancement. Upon irradiation the sample surface became smoother: roughness probed by atomic force microscopy (AFM, Veeco Autoprobe M5) on a scale of 1 µm yielded 15 and 6 nm rms for the plain and implanted samples, respectively. Note that for niobium the effect is opposite [17]. On the other hand, the irradiation did not change the large-scale profile formed by the spark cutting: average valley-to-hill height and distance were 0.2 and 2 µm, respectively. Using Rutherford backscattering and channelling spectrometry with a 1.57 MeV He$^+$ beam, the damage accumulation in the sample was analysed. It was found that due to the Xe irradiation, the crystalline structure is degraded in a surface layer with thickness of approximately 50 nm.

To construct the phase diagram of the surface-enhanced samples, dc magnetization was measured versus in-plane magnetic field at temperatures from 3.76 K down to 2 K, using a Quantum Design SQUID magnetometer. Magnetization data of the plain sample served as a reference. The data for the implanted sample for decreasing and increasing magnetic field at supercritical temperature 3.74 K are shown in figure 1. Experimental curves for the plain and polished samples, for decreasing field, are shown for comparison. The supercritical magnetization is much greater than fluctuation diamagnetism [13]; on the other hand, it is three orders of magnitude smaller than the magnetization measured at 3.72 K. The standard deviation of the temperature and magnetic field readings is 0.005 K and 0.005 Oe, respectively. The inhomogeneity of the magnetic field on a 3 cm scan length, used in the measurements, is 0.05%. The uncertainty on the data for the magnetic moment $M$ is $\pm 1 \times 10^{-7}$ emu.

**Figure 1.** Magnetization at supercritical temperature 3.74 K. Open and closed circles are for the implanted sample for decreasing and increasing field, respectively; $H_s$ is the maximum field for surface superconductivity. In the inset, $-M$ is shown on a semi-log scale.
Onset and vanishing of surface superconductivity occur with noticeable hysteresis (see also [13]), which is consistent with an underlying first-order phase transition. This can be seen more clearly in the data shown on semi-log scale in the insert of figure 1. The origin in figure 1 is shifted with respect to zero field due to a small residual field in the magnetometer. For consistency only data obtained at positive fields are discussed. A maximum field, at which surface superconductivity is recognizable, is reached for increasing field and marked as $H_s$. Note the difference with respect to conventional surface superconductivity at $H_{c3}$; the latter develops as a second-order phase transition and does not involve hysteresis.

The subcritical $M(H)$ isotherms can be divided into high- and low-temperature groups, with and without surface superconductivity, respectively. The absence of the surface sheath at low temperatures and its presence at higher ones is a hallmark of the wetting transition.

Typical magnetization data near the bulk critical field for two isotherms from the high- and low-temperature groups are shown in figures 2(a) and (b), respectively. $H_c$ marks the field of the bulk transition to the normal state. This transition takes place at the same field for all three samples. There is no apparent metastable continuation of bulk superconductivity, so $H_c$ is the thermodynamic critical field. $H_s$ for the implanted sample is only barely different from that for the polished sample.

In figure 2(a), surface superconductivity in the polished and implanted samples is clearly noticeable for increasing field ($H_c < H < H_s$). For decreasing field the range of metastable continuation of the surface normal state increases with decreasing temperature; at $T = 3.64 \text{ K}$ the surface normal state in the implanted samples persists down to $H_c$, and at $3.54 \text{ K}$ the normal state metastability in both surface-enhanced samples extends below $H_c$. No surface superconductivity was recorded for the plain sample. The range of normal state metastability for the plain sample is larger than that for the surface-enhanced samples. The difference $\Delta H = H_s - H_c$ gradually decreases with decreasing $T$.

As is seen from figure 2(b), at low $T$ no surface superconductivity was recorded. The normal state metastability range in the plain sample increases with decreasing $T$; the same occurs in the polished sample, but for a smaller range. Normal state metastability is barely noticeable
in the implanted sample. This may be due to the greater uniformity of surface defects created by irradiation.

The phase diagram of the implanted sample constructed from the magnetization data is shown in figure 3. First, we compare our results for \( H_c(T) \) with classic data \([18]\), depicted with crosses. There is a systematic shift of less than 2 Oe in field and, correspondingly, 0.01 K in temperature between the coexistence curve (solid line) and those data.

As figure 3 shows, the phase diagram of surface-enhanced Sn is different from the standard phase diagram of low-\( \kappa \) type-I superconductors and consistent with that predicted in \([2]\). The critical temperature for surface superconductivity in zero field is \( T_{cs} \approx 3.78 \) K. Linear extrapolation of the \( H_s \) data towards low \( T \) yields a location \( W \) of the wetting transition at \( T_w \approx 3.25 \) K.

In the inset \( H_s(T) \) for implanted and polished samples are shown as \( \Delta H \equiv H_s - H_c \) versus \( T \). The curve is the well-known theoretical dependence \( \Delta H \propto -(T - T_w)/\ln(T - T_w) \) for the prewetting curve close to \( W \), for systems with short-range interactions,\(^3\) originally derived in \([19]\) and confirmed for superconductors in \([10]\). The fit to \( \Delta H(T) \) for the implanted sample yields the improved estimate \( T_w \approx 3.10 \) K.

The global phase diagram (\( \kappa \) versus \( \xi(T)/b \), with \( \xi(T) \) the GL coherence length) derived in \([2]\) allows one to infer \( \kappa \) from parameters of surface and bulk superconductivity. To check this prediction, we first calculate \( \kappa \) for the implanted sample, using the standard procedure following the well-known formula \([21]\) \( \kappa = \kappa_p (1 + 0.78 \xi_0/l) \), where \( \kappa_p \) is the GL parameter in the pure limit, \( \xi_0 \) the Pippard or Bardeen–Cooper–Schrieffer (BCS) coherence length, and \( l \) the electron mean free path. The latter was obtained from the residual resistivity ratio (RRR) at 293 K and 6 K,\(^3\) However, ‘long-range’ dispersion forces may complicate the picture, even in superconductors. See \([20]\).

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measured using the van der Pauw technique. RRR for the plain sample is 120, and RRR measured for the modified side of the implanted sample is close to 40. Since surface superconductivity develops in a much thicker layer than just the layer with degraded crystalline structure, we have to use the mean free path for the bulk, i.e., the value found for the plain sample. Other quantities used are: 1.03 × 10^{-11} \, \Omega \, \text{cm}^2 for l/\sigma \, [14], 8.9 \times 10^{4} (\Omega \, \text{cm})^{-1} for the electrical conductivity \sigma at room temperature [15], 3100 Å for \xi_{0} [11], and 0.15 for \kappa_{p} [14]. We find l = 1.2 \times 10^{4} \, \text{Å}, and \kappa \approx 0.18.

Next, we deduce \kappa from the global phase diagram (see figure 2 of the first paper of [2]). We need to calculate \xi(T_{w})/b. According to the theory \( b = -\xi(T_{cs}) \), so \( \xi(T_{w})/b = -\sqrt{(T_{cs} - T_{c})/(T_{c} - T_{w})} \). Taking for \( T_{c} \), \( T_{cs} \), and \( T_{w} \), 3.73, 3.78 and 3.25 K, respectively, we obtain \( \kappa \approx 0.18 \), while, taking \( T_{w} = 3.10 \, \text{K} \), we find \( \kappa \approx 0.20 \). Both estimates agree well with that found by the standard procedure. Moreover, we find that assuming \( \kappa \approx 0.2 \) the entire prewetting line closely follows the calculated one shown in figure 3 in the first paper of [2].

Thus, the theory [2] agrees quantitatively with experiment as regards the first-order prewetting line and the value of \( \kappa \). The magnetization data at \( T > T_{c} \) (e.g., figure 1) allow us to make one more estimate. The slope \( \partial M/\partial H \) at zero field is proportional to the volume of the superconducting sheath, and therefore to its effective thickness \( d \). Calculations for the implanted sample yield \( d \approx 10 \, \mu \text{m} \) for 3.74 K and \( d \approx 1 \, \mu \text{m} \) for 3.76 K. These thicknesses are of the order of \( \xi(T) \) and largely exceed that of the damaged layer (50 nm). The sheath disappears at \( T_{cs} \). Our findings are consistent with the prediction that, for \( T > T_{cs} \), the superconducting order parameter decays into the sample on the scale of \( \xi(T) \propto (T - T_{c})^{-1/2} \), and its amplitude vanishes at \( T_{cs} \).

Below \( T_{cs} \), in the complete wetting regime \( T > T_{cs} \), theory predicts a very weak divergence of the sheath thickness upon lowering \( H \) towards \( H_{c} \), of the form \( \ln(1/(H - H_{c})) \) [2]. The data (figure 2(a)) allow us to detect wetting layer thicknesses up till about a few \( \mu \text{m} \), slightly larger than \( \xi(T) \) at the temperatures under consideration. Fits to our data agree better with the predicted logarithmic divergence than with a power law.

Finally we estimate \( b \), using \( \xi^{-1}(T) = \xi_{p}^{-1}(T)(1 + 0.86 \, (\xi_{0}/l)^{-1/2}) \), where \( \xi_{p}(T) \) is the pure limit of \( \xi(T) \) [3]. We obtain \( b = -1.4 \, \mu \text{m} \approx -5\xi_{0} \).

We arrive at the following conclusions. (1) The observed \( H-T \) phase diagram for a surface-enhanced Sn type-I superconductor differs qualitatively from the standard phase diagram for superconductivity and is consistent with that predicted for low-\( \kappa \) type-I superconductors undergoing an interface delocalization transition. (2) Onset of surface superconductivity in surface-enhanced samples occurs as a first-order phase transition at \( T > T_{w} \). There is no surface superconductivity at \( T < T_{w} \). The surface transition \( H_{s}(T) \) disappears at a surface critical temperature \( T_{cs} > T_{c} \). (3) Surface enhancement of superconductivity in Sn can be induced in a controllable way by different kinds of surface cold working, such as irradiation by ions of, e.g., heavy noble gases, or mechanical polishing.

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