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Surface enhancement of superconductivity in tin

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The possibility of reversible surface enhancement of superconductivity is examined experimentally. It is shown that single crystal tin samples with cold-worked surfaces represent a superconductor with a surface-enhanced order parameter (or negative surface extrapolation length), whose magnitude can be controlled.

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Properties of superconductors with surface enhancement of the order parameter, i.e., with a negative value of the extrapolation length b in a generalized boundary condition within Ginzburg-Landau theory,[1] are a subject of long-standing discussions. Fink and Joiner[2] suggested, for the first time, that such a boundary condition should lead to an increase of the surface critical temperature of semi-infinite samples in zero magnetic field. This means that the shape of the phase diagram for surface-enhanced superconductors may differ qualitatively from the classical one, for which both the bulk and the surface superconducting transitions have the same critical temperature, T_c, and there is no stable superconductivity above the critical point. We recall that the classical shape of the phase diagram is valid if the order parameter at the sample boundary has zero slope ($b=\infty$) or decreases ($b>0$), which is appropriate for superconductor/vacuum or superconductor/normal-metal interfaces, respectively.[1,3] Fink and Joiner have also shown experimentally that cold working the surface of a type-I superconductor ($In_{0.993}Bi_{0.007}$ alloy) increases the superconducting transition temperature, which they interpreted as a result of the surface enhancement. The observed shift in the critical temperature was about 0.02 K (T_c for this alloy is 3.5 K).

Khlyustikov and Khaikin carried out an extensive experimental study of anomalous superconductivity at supercritical temperatures in pure metals, which is reviewed in Ref. 4. They found that mechanical treatment, such as bending and polishing, of carefully annealed single-crystal samples of some metals (Sn, In, Nb, Re, and Tl) increases the critical temperature, whereas other metals (Al and Pb) do not show this effect. A maximum shift in the critical temperature of 0.04 K was observed in tin. However, in contrast to Fink and Joiner, Khaikin and Khlyustikov interpreted their observations in terms of twinning-plane superconductivity occurring either in the interior or on the surface of the sample.[5] Twinning is the formation of two single-crystal regions (twins) so that the planar boundary between the twins is one of the crystallographic planes of the crystal. An important feature of twinning planes is that they do not involve stresses and therefore are not affected by annealing. Buzdin developed a Ginzburg-Landau theory of superconductivity in crystals with planar defects displaying enhancement of superconductivity, by incorporating negative b. The theoretical results are in agreement with the experimental data.[4]

Indekeu and van Leeuwen[6] studied the consequences of surface enhancement in type-I superconductors of semi-infinite geometry within Ginzburg-Landau theory. An interface delocalization or "wetting" transition for surface-enhanced type-I superconductors was predicted. The transition is of first order for superconductors with low values of the Ginzburg-Landau parameter κ (below 0.374), and of second order for the higher-κ superconductors ($0.374<\kappa<1/\sqrt{2}$). In both cases nucleation of surface superconductivity in zero field should occur above the bulk critical temperature. It was also shown that the surface phase diagram for low-κ superconductors has the same shape as for crystals with planar internal defects, regardless of the character of the defects (quantified by the transparency of the planar boundary to electrons).[7] In other words, at low κ the Ginzburg-Landau theory does not distinguish between a free surface, a grain boundary, or a twinning plane.

Thus we face a dilemma: the same experimental results can be interpreted in two principally different ways: either as an effect of *stresses* induced by surface treatment[2] or as the effect of *stress-free* defects.[5] For this reason it is interesting to examine which one of these interpretations is correct, or if both effects coexist, which one is dominant. Resolution of this dilemma constitutes the purpose of this paper. Another motivation is associated with the prediction of wetting phenomena in superconductors. For its verification one has to find a surface modification providing an enhancement of the order parameter with controllable magnitude of the *negative* extrapolation length b. Associated with this is the prediction that surface enhancement can yield a significant (up to a factor of ten in units of $T_{cs}-T_c$, where T_{cs} is the surface critical temperature of a semi-infinite system) increase of the critical temperature for samples with dimensions of the order of 1 μm.[8,9] If this is confirmed, surface enhancement may find practical applications.

The experiments have been carried out with tin, because to our knowledge it exhibits the strongest anomalous superconductivity above T_c.[4] The first samples we tested were cut from a high purity (99.9998%, Alfa Aesar) tin foil of 0.1 mm thickness, fabricated by cold rolling. The sample area was 5×7 mm^2. After overnight annealing (about 10 hours) at 200 °C in vacuum ($\sim10^{-6}$ mbar), DC magnetization was measured with a commercial SQUID magnetometer (Quantum Design, typical error for the temperature readings is ±0.005 K) in a parallel magnetic field at temperatures above and below the bulk critical temperature T_c [$T_c=3.722$ K (Ref. 10)]. For brevity these specimens will be referred to as "standard."

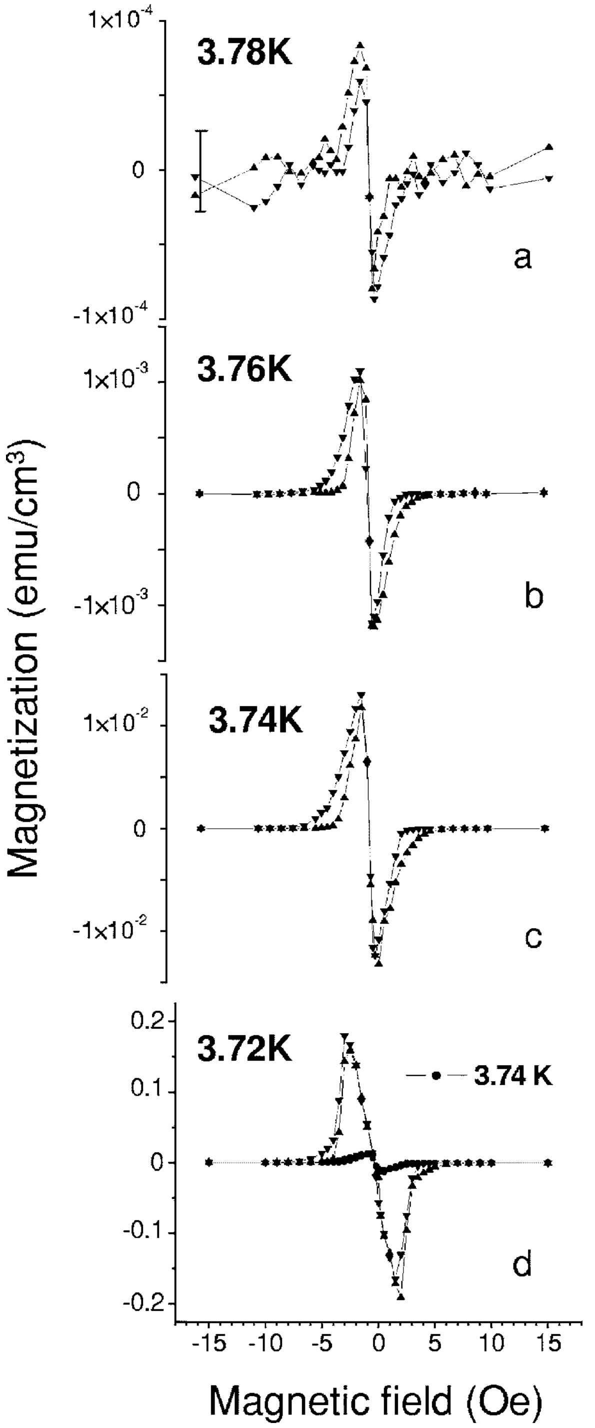

FIG. 1. Magnetization of the standard tin foil at supercritical [(a), (b), and (c)] and subcritical (d) temperatures. Down triangles are experimental points obtained for decreasing field, and up triangles are for increasing field. The error bar in (a) indicates average noise level, corresponding to $\pm 1 \times 10^{-7}$ emu. Points for temperature 3.74 K (solid circles) are repeated in (d) for comparison.

Results of the measurements for three supercritical temperatures and one subcritical temperature are shown in Fig. 1. The background magnetization from the sample holder was measured at 3.82 K and was subtracted from the data taken at lower temperatures. For the standard samples a distinct diamagnetic response was recorded starting from 3.78 K. The diamagnetic moment is several orders of magnitude (four orders for 3.74 K) stronger than that expected for fluctuation diamagnetism.[3] So we doubtlessly deal with the phenomenon of interest, stable superconductivity above the bulk critical temperature, which was first revealed in Refs. 11 and 12 and studied in Ref. 13 for single crystal tin samples. However, in our case the effect is significantly stronger. In particular, the amplitude of the anomalous diamagnetic response reported in Ref. 13 for 3.76 K in terms of magnetization is about 5×10^{-5} emu/cm^3; in our case it is 1.2×10^{-3} emu/cm^3. Hysteresis for decreasing and increasing magnetic field is conspicuous for all temperatures, which indicates supercooling at nucleation of anomalous superconductivity, and is attributed to a first-order phase transition. This is in agreement with the observations of Khlyustikov and Khaikin, which are reviewed in Ref. 4.

The slopes $\partial m / \partial H$ (m is the magnetization in emu/cm^3, and H is the magnetic field in Oe) for subcritical isotherms at low fields have the same value close to $1/4\pi$, as expected for the Meissner state. The low-field slope for the supercritical isotherms decreases with temperature, allowing one to estimate the volume fraction of the anomalous superconducting phase. Such an estimate yields 0.5% at 3.78 K, 5% at 3.76 K, and up to 40% at 3.74 K.

Obviously, this amount of superconducting phase is too big to be consistent with superconductivity on the sample surface alone. As an additional check, the magnetization was measured after polishing one and then also the other side of the sample. The magnetization exhibited an increase of about 10 to 20% only, after polishing one side. These results are definitely in favor of the bulk (sample interior) origin of the observed anomalies. On the other hand, so big a fraction of anomalous superconducting phase can hardly be consistent with twinning-plane superconductivity alone, in view of the delicate nature of twinning.

Examining the foil samples with an optical microscope (Jenavert, Sypac s.c.s.), we noticed that the cold-rolled foil consists of flake-like grains with a typical size of the order of 10 μm, and a thickness of the order of 1 μm. A photograph of the foil surface is shown in Fig. 2(a). The grains appear to be rather weakly bonded, since the foil can be disintegrated by agitation in an ultrasonic bath. Therefore, the real surface area is the sum of the grain surfaces, which is much larger than the area of the sample outer surface. Measurements of the magnetization of an ultrasonically ground foil (one-hour exposure in a commercial ultrasonic bath (Branson 5200); the sample was in a beaker with acetone at room temperature) yielded an anomalous signal similar to that shown in Fig. 1, but with a magnitude smaller by about a factor of three. Foils annealed for a long time (70 hours) and at a high temperature (230 °C) also yielded an anomalous magnetization lower by a similar factor.

In Fig. 3 the data taken at 3.76 K for the annealed and the ground Alfa Aesar (AA) foils are compared with that for the standard foil. The graph also contains data obtained with a home-made foil of 0.2 mm thickness. This foil was fabricated via remelting AA-foil between glass plates in vacuum ($\sim 10^{-5}$ mbar). The surface of the remelted foil, shown in Fig. 2(b), has a smooth mirrorlike finish, replicating the sur-

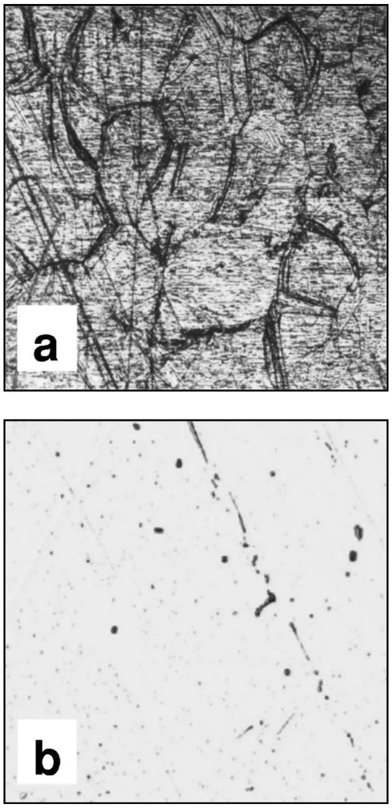

FIG. 2. Photographs of the surface of the tin foils. (a) Alfa-Aesar cold rolled foil. (b) Home-made foil (Alfa-Aesar foil remelted in vacuum). The size of the images corresponds to 60 μm.

face of the glass plates. No grains are visible, and ultrasonic agitation does not destroy the foil. Therefore we conclude that the remelted foil possesses a uniform polycrystalline structure. The remelted foil exhibits essentially the same anomalous diamagnetic response before and after annealing. This response is much stronger (by a factor of 50) than that observed in annealed single-crystal samples (experiments with single crystals are discussed below).

The data obtained for the standard and annealed AA-foils demonstrate that the major part (two-thirds) of the anomalous superconductivity is due to stressed defects. The fact that we obtained similar results for the annealed and ultrasonically ground samples allows us to conclude that the stresses concentrate at the interfaces between the grains: disintegration relaxes the stresses. If so, the major part of the anomaly might be assigned to surface enhancement of superconductivity in the grains. Equality of the diamagnetic response of the annealed and ground AA-foils to that of the remelted foil on one hand, and much smaller magnitude of the anomaly in single-crystal samples on the other hand (see below) indicate that the remaining one third of the superconductivity enhancement in foils is associated with their polycrystalline structure. In view of the random orientation of crystallites in polycrystals it is unlikely that twins make any visible contribution to the anomalous superconductivity of these samples. Clarification of the specific mechanism responsible for enhancement of superconductivity in polycrystalline tin is a very interesting problem, which is, however, out of the scope of the present work. Since our present goal is to achieve a pure surface enhancement, it is clear that polycrystalline samples are not appropriate. For that reason subsequent experiments were performed with single-crystal samples.

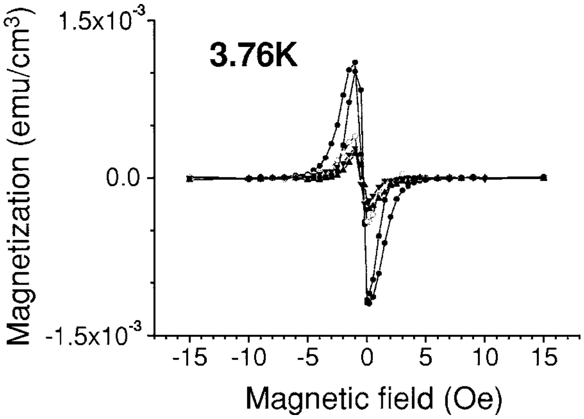

FIG. 3. Anomalous magnetization in different tin foils. Solid circles, open circles, and solid triangles represent the standard, annealed, and ultrasonically ground cold-rolled foils, respectively. Solid squares represent the remelted foil.

The single-crystal samples (Alfa Aesar, cast from 99.9999% pure tin) had a disk shape about 7 mm in diameter and 1 mm in thickness. We worked with two samples. Sample no. 1 was first annealed at 230 °C for 100 hours and then polished on both sides with a silicon carbide grinding paper no. 4000 (Struers S.A.S., grain size 5 μm). Sample no. 2 was first polished, then annealed and then polished again. dc magnetization has been measured after each of these steps. The chosen annealing temperature, 230 °C, turned out to be optimal to provide sufficiently close proximity to the melting point (232 °C) without significant risk of sample overheating at the temperature stabilization.

Anomalous magnetization of sample no. 1 in the annealed state was not observed down to 3.76 K. At 3.76 K and 3.74 K its amplitude was 2×10^{-5} and 2×10^{-4} emu/cm^3, respectively, which, as already mentioned above, is much lower than that observed for the foils. After polishing, the magnetization of sample no. 1 increased by a factor of 5 to 6.

The magnetization data obtained for sample no. 2 are shown in Fig. 4. After annealing, the magnitude of the anomaly dropped by a factor of ten; then it was completely restored by repolishing.

We also checked if annealing-polishing procedures affect the bulk transition temperature via measurements of the temperature dependence of the magnetization near T_c in a field of 0.5 Oe for polished sample no. 1 and annealed sample no. 2. Results are shown in Fig. 5. The magnetization at the foot of the transition is shown in the insert on enlarged scale. There is no visible change in the bulk transition temperature, while the foot does change both in magnitude and in temperature width. In the polished sample the foot is higher and wider. This is an additional confirmation of surface enhancement of superconductivity by cold working the sample surface.

Thus we arrive at the following conclusions. (a) The anomalous superconductivity in both polycrystalline and

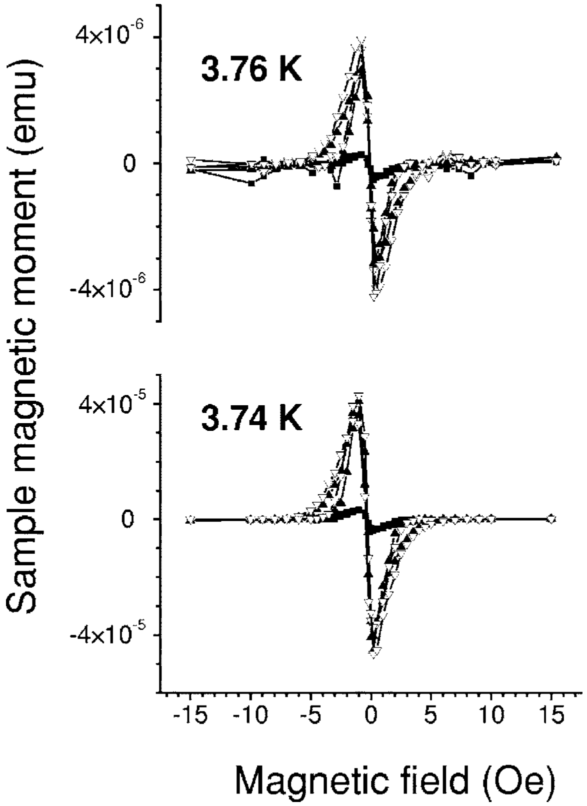

FIG. 4. Magnetic moment of the polished (solid triangles), annealed (solid squares), and repolished (open triangles) single-crystal sample no. 2.

single-crystal tin samples is mainly hosted by *stressed* defects. (b) Surface superconductivity in tin can be induced using mechanical polishing (surface cold working). The twinning-plane interpretation of this phenomenon suggested in Ref. 5 is not adequate. (c) The nucleation of surface superconductivity occurs as a first-order phase transition. (d) Single-crystal tin samples with polished surfaces represent a superconductor with surface-enhanced order parameter and, correspondingly, with negative extrapolation length b. (e) The enhancement strength (or magnitude of b) can be *controlled*, for instance, by manipulating the abrasive grain size and the annealing parameters (time and temperature). This point requires further study, however.

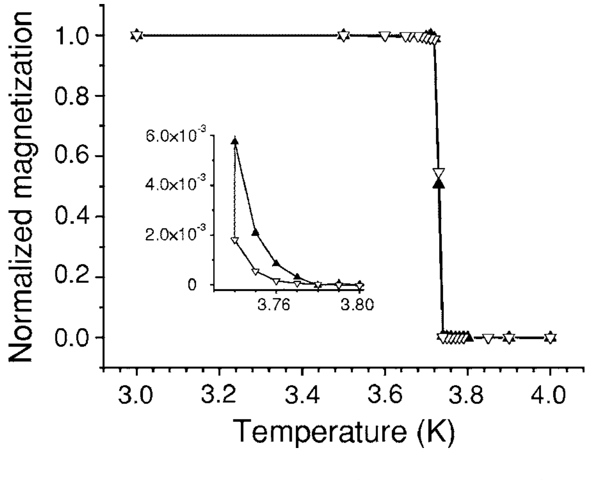

FIG. 5. Normalized magnetization (with reversed sign) for the annealed (open triangles) and polished (solid triangles) single crystal tin samples at 0.5 Oe. The inset shows the magnetization near the foot of the transition.

We believe that the residual anomalous magnetization measured in the single-crystal samples could be further reduced by annealing at closer proximity to the melting point. However, it is possible that a *minor* part of the anomaly comes from internal low-stress defects, most probably of the same nature as those responsible for anomalous superconductivity in polycrystalline tin.

Finally, the fabricated surface-enhanced single-crystal tin samples provide a reproducible basis for setting up an experimental verification of the theoretically predicted interface delocalization phenomena in type-I superconductors. Related to this phenomenon is the capillary condensation in meso-sized samples, and the concomitant important increase of T_c.[8,9] In this context it is interesting to note that the obtained data are consistent with this theory. Specifically, the fact that the temperature at which the anomalous superconductivity occurs in the cold-rolled foil samples is higher than that for the single crystals supports this prediction, taking into account that the foil consists of relatively small grains. Of course, this reasoning should be considered as speculative rather than as an argument in view of the large difference between the grains in foils versus the slabs, cylinders and spheres discussed in the theory.

An important question remains. What kind(s) of stressed defects are responsible for the observed enhancement of superconductivity in single crystals? Since we applied polishing, which is surface cold working, one could assume that the defects are mainly dislocations and intercrystallite boundaries, which can be strongly stressed (see, e.g., Ref. 4). Then a kind of standard explanation is that the stresses build up regions of local tension and compression with enhanced superconductivity. But in order to be consistent, this requires increasing T_c for both the tensile and compressed states. However, according to available data[14] T_c of tin *decreases* under compression. Although we are not aware about experimental data on superconductivity in tensile tin, it is obvious that an interpretation in terms of dislocations and/or stressed intercrystallite boundaries is not readily applicable to our observations. On the other hand, one can envision an alternative approach associated with the well-known enhancement of superconductivity occurring in disordered films of many nontransition metals.[15,16] In particular, it was observed that T_c in amorphous (quench-condensed) tin films increases by as much as 0.7–1.0 K. This increase is usually attributed to a modification of the phonon spectrum due to disorder.[15,17] Thus one might speculate that the reported surface enhancement is induced by a partial disorder produced by polishing. The observed much smaller change of the critical temperature is not surprising in view of the different degree of disorder and the proximity coupling to the normal metal. It is also possible that disorder at the intercrystallite boundaries is causing the enhancement of superconductivity in polycrystalline samples. Yet another route towards superconductivity enhancement is known for granular films.[18] These films are fabricated via vapor deposition in a low-pressure oxygen atmosphere. At some deposition rates and particular oxygen pressure, resulting in specific grain size and thickness of oxide coating of the grains, such films can show significant increase in T_c (for Al films studied in Ref. 18 this increase was close to 1 K). However, the "granular-film" interpretation of our results is not plausible (at least not in the sense of a major contribution), because the superconductivity enhancement, which could be reached via oxidation, should not be affected by annealing. One more contribution might be associated with the influence of surface phonons due to surface modification, as demonstrated by Naugle *et al.*[17] However, such an effect is very small and requires thin films (~ 10 nm) to become visible. The issue of the origin of the reported observations clearly requires additional studies.

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