Influence of defects on the critical parameters of twinning plane superconductivity

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The dependence of the critical parameters of twinning plane superconductivity (TPS) in tin on defect concentration in the twinning plane (TP) is measured. The angle α at the vertex of the twinning wedge arising from mechanical twinning of the single-crystal specimen was used to estimate defect density. It is determined that as α diminishes from $\sim 10^{-2}$ rad the critical temperatures of TPS diminish and for $\alpha < 5\text{–}6\cdot 10^{-4}$ rad they drop below the critical temperature of bulk superconductivity. An estimate of the limiting values of the critical temperatures of TPS for $\alpha = 0$ has demonstrated that in this case they are ~ 0.02 and ~ 0.05 K below the bulk superconductivity critical temperature. It is established that all specimens containing twinning planes have a region on the H, T-phase diagram corresponding to spatially inhomogeneous superconducting states of the twinning planes identified in Ref. 1.

INTRODUCTION

The H, T-phase diagram of the superconductivity of tin crystals containing twinning planes (TP) has been investigated in detail in previous studies.[1,3] The specimens for these experiments were fabricated at room temperature and above. A sample H, T-phase diagram characteristic of such specimens is given in Fig. 1a (Ref. 1). Compared to the phase diagram of ordinary bulk superconductivity the phase diagram of the superconductivity of specimens with TP contains an entire series of new critical magnetic lines.

The critical parameters of bulk superconductivity are well-known. For type-I superconductors, which includes tin, these are the critical temperature T_{c0} and the critical magnetic fields: $H_c(T)$, the thermodynamic equilibrium field between the normal and superconducting states; $H_{c2}(T)$, the field due to supercooling, an absolute instability of the normal state; $H_{c3}(T) \approx 1.7\, H_{c2}(T)$, the critical field of surface superconductivity (under certain conditions the supercooling field plays this role); and $H_{c1}(T)$, the field due to superheating, an absolute instability of the superconducting state.

The critical parameters of bulk superconductivity such as T_{c0} and $H_c(T)$ are convenient for use as reference parameters. The measurement results for these quantities with the corresponding designations are shown in Fig. 1. The figure also provides the critical magnetic field $H_{c3}(T)$ for comparison purposes.

Analysis of tin specimens containing twinning planes reveals a significantly more complex transition to the superconducting state in these specimens. First at a critical temperature T_c above T_{c0} there exists a transition to a state characterized by an anomalous diamagnetic moment. Since relations that can clearly be interpreted as supercooling are observed in a finite magnetic field this suggests a first-order phase transition.[2] The critical magnetic fields of this transition are the fields $H_d(T)$, the critical magnetic field of thermodynamic equilibrium between the normal and superconducting states of the twinning plane and $H_m(T)$, the critical supercooling field, the absolute instability of the normal TP state. Moreover investigations of bulk superconductivity supercooling have revealed two additional critical magnetic field lines that differ from $H_{c2}(T)$ and $H_{c3}(T)$. These include the critical magnetic field $H_b(T)$ below which the bulk of a specimen containing TP cannot be supercooled by demagnetization from strong fields [exceeding $H_d(T)$] and the critical magnetic field $H^*(T)$: the supercooling field of the bulk in the absence of twinning plane superconductivity (TPS). Extrapolation of $H_b(T)$ to intersection with the temperature axis yields the second critical temperature of TPS: T_b. Both critical temperatures and all critical magnetic fields of TPS are also shown in Fig. 1a. It is important to note that in measuring the magnetic properties of specimens containing twinning planes the critical magnetic field of TPS $H_b(T)$ and the portion of the relation $H_m(T)$ lying below $H_c(T)$ are registered as the supercooling field of the entire specimen.

It should be pointed out that all the experiments employing tin have also revealed superheating of the superconducting state of the specimens. However, since the shapes of the specimens deviated so substantially from ellipsoidal

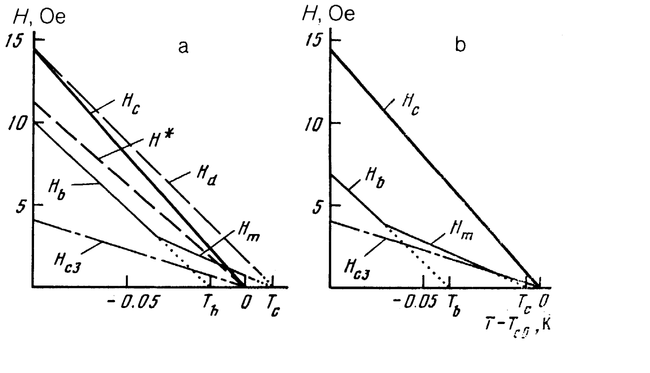

FIG. 1. Phase diagrams of the superconductivity of tin specimens containing twins: a—$\alpha = 1.4\cdot 10^{-3}$ rad, b—$\alpha = 1.2\cdot 10^{-4}$ rad. The critical magnetic field $H_{c3}(T)$ line was plotted based on measurements of single crystal control specimens; α: Angle at the vertex of the twinning wedge.

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form, quantitative processing of the measurement results of the superheating fields was very nearly impossible. Hence the phase diagrams given here do not contain results of superheating observations.

The analysis of the properties of TP specimens carried out in Ref. 1 based on a comparison with known observed properties of bulk and surface superconductivity has suggested that the superconducting state of the twinning planes is spatially inhomogeneous between the $H_b(T)$ and $H_d(T)$ lines on the phase diagram; this state is characterized solely by short-range order in the absence of long-range order (naturally we refer to the directions along the twinning planes).

A number of different causes can be proposed to explain the spatial inhomogeneity of the superconducting state of TP. The primary purpose of the present study was to consider the role of one such cause; specifically, the role of the naturally-occurring TP defects in actual specimens. The data from Ref. 4 suggest that the twinning planes that ordinarily arise upon mechanical twinning of tin at near-room temperature will contain approximately one defect per 100 interatomic distances. This was responsible for the tendency of the present study to attempt to achieve as perfect and defect-free a TP structure as possible.

Preliminary data that TP defects have an effect on the observed TPS characteristics can be found in Ref. 2. This study has pointed out that in order to make it possible to unambiguously determine the critical magnetic fields of TP $H_d(T)$ and $H_m(T)$, it is necessary to have specimens with a perfectly uniform (at least for optical analysis) path of the twinning planes to the external surface of the specimen. Otherwise when the intersection of the TP with the outer surface reveals bends of some type, i.e., when the specimen contains TP with different defect densities, it is necessary to analyze a broad range of values for each of the TPS critical fields in order to describe the properties of these specimens.

FABRICATION OF SPECIMENS AND EXPERIMENTAL TECHNIQUE

The phenomenon of TPS has been identified in a wide range of metals today, although tin remains the most convenient material for research. This can be attributed to the fact that, first, a high-quality single crystal is comparatively easy to grow from tin and can be used as the initial preform for fabrication of the specimens; second, tin has a "proclivity" for twinning under plastic deformation; and, third, it is possible to observe TPS in a rather convenient temperature range that is comparatively easily achieved.

Tin single crystals in the form of cylinders ~ 8 mm in diameter and ~ 100 mm in length were used in the present study as preforms for fabricating the specimens. The (301) crystalline plane coincided with the axis of the cylinders. Orientation of the crystallographic axes of the preforms was maintained accurate to $\sim 1°$. X-ray monitoring of the orientation of the grown single crystals was used. Mechanical twinning of the preforms was initiated by striking the end face of the preforms with a blade whose plane was parallel to the (301) plane. This produced wedge-shaped regions of twinning orientation in the single crystal.

The angle α at the vertex of the twinning wedge was used as the characteristic. Reference 5 has demonstrated that the primary TP defects producing the finite angle α under mechanical twinning are the ridges one interatomic distance in height separating the atomically-smooth TP regions. This viewpoint is confirmed by direct electron microscope observations which have been carried out in, for example, Ref. 4.

By employing mechanical twinning at different temperatures it is possible to obtain twins with different characteristic angles α. Variations in α from $\sim 10^{-5}$ to $\sim 10^{-2}$ rad were found to correspond to temperature variations in mechanical twinning from liquid nitrogen temperatures through room temperature. This made it possible to fabricate a series of specimens with substantially different values of α. The control specimens were cleaved from the single crystal sections of the same preforms.

The essential difference between the specimen fabrication technique used in the present study compared to that employed in Ref. 1 lies in the use of polishing etching to remove the surface metal layer contaminated through electrical erosion treatments. Three concentrated acids—nitric, hydrochloric and perchloric—were used for the polishing etching process in a volume ratio of 1.5:1:1, respectively. Dewatered ethylene glycol was used for the initial washing of the polished specimen; this was followed by washing with distilled water.

The experimental technique and the routine based on measurements of dependences of the magnetic moments of the specimens of the magnetic field at a number of fixed temperatures used in the present study are identical to those employed in Ref. 1. The H, T-phase diagrams of the specimens were recovered from measurements of magnetic fields corresponding to the features of the $M(H)$ relations obtained.

EXPERIMENTAL RESULTS

As noted above the TPS properties were determined in Ref. 1 based on comparison of the properties of specimens containing twins with the known properties of bulk and surface superconductivity. Therefore in the present study we shall briefly describe the experimental results with the single crystal control specimens.

The measurements were carried out over a temperature range from 4.2 to ~ 3.0 K. All magnetic moment relations of the control specimens were in complete agreement with classical relations characteristic of superconductivity. At subcritical temperatures ($T_{c0} \approx 3.7$ K for tin) we observed magnetic field-induced loss of superconductivity, supercooling of the normal state and superheating of the superconducting state. Quantitative processing of the measurement results of the critical magnetic fields $H(T)$ and the supercooling field has revealed that supercooling is observed across the entire temperature range up through the critical field $H_{c3}(T)$ which can be expected since no special measures were taken to suppress surface superconductivity. Numerical measurement results for the fields $H_c(T)$ and the supercooling fields were in agreement with Ref. 6. Measurements of the superheating fields which were processed accurate to only an order of magnitude (since the test specimens were far from ellipsoidal in shape), are also in agreement with existing literature data on tin.

Supercooling up through the field H_{c3} could be achieved only by using polishing etching. This is because smooth surfaces are substantially more resistant to external mechanical action than are rough fields. Microcusps on a rough surface deform quite easily and therefore microscopic defects that are difficult to identify, including twins, are easily induced in the specimen. It was not possible to observe supercooling to the critical field H_{c3} in any of the experiments on specimens with a rough surface.

In all cases the specimens containing twinning planes differed in their properties from the control single crystals. It was determined that the critical parameters of TPS are dependent on the defect concentration on the twinning planes. It was also possible to identify the properties of TPS that remained unchanged from specimen to specimen. Such characteristics include the temperature derivatives of the critical magnetic fields $dH_d(T)/dT$, $dH_m(T)/dT$ and $dH_b(T)/dT$ of TPS.

Figure 2 shows the results from numerical differentiation of the relations of the critical supercooling fields of the normal state in the bulk of the specimens at temperatures below T_{c0}. The data shown in Fig. 2 were obtained from three specimens, one of which was the control, while the other contained a twin with $\alpha = 1.4\cdot10^{-3}$ with the third containing a twin with $\alpha = 1.2\cdot10^{-4}$. The high measurement accuracy near T_{c0} was achieved by virtue of the fact that the temperature was determined by the known $H_c(T)$ relation. The right side of the figure contains labels corresponding to the known[1] values of the derivatives of the critical fields H_{c3}, H_m, and H_b.

The absence of a dependence of the temperature derivatives of the critical magnetic fields of TPS on the angle α was used as the criterion for identifying the observed features in the phase diagrams of superconductivity of specimens containing twinning planes.

Figure 1a, shows the H, T-phase diagram of superconductivity of a specimen containing a twin with $\alpha = 1.4\cdot10^{-3}$. This figure was used previously in the present study to describe the observed critical fields. Figure 1b, shows the phase diagram of a specimen with $\alpha = 1.2\cdot10^{-4}$. Only $H_c(T)$ and the supercooling field were observed for this specimen. The measured temperature dependence of the supercooling field contains three linear sections which, based on the criterion noted above, were determined to correspond to the critical fields $H_b(T)$, $H_m(T)$, and $H_{c3}(T)$. The critical temperatures of TPS T_c and T_b in this case were determined by extrapolation of the $H_m(T)$ and $H_b(T)$ lines, respectively, to intersect with the temperature axis. The H_{c3} lines in Figs. 1 a,b, were obtained from measurements on the single-crystal control specimens.

A fundamentally new element reflected in Figs. 1 a, b, is that the critical temperature of TPS T_c as a function of the angle α may lie both above and below the bulk-superconductivity critical temperature T_{c0}. The temperature T_c was above T_{c0} for specimens with comparatively large angles α while the situation was reversed for specimens with comparatively small angles α.

Measurement results for the critical temperatures of TPS T_c and T_b obtained on different samples are shown in Fig. 3. The proximity of four points obtained on different samples with $\alpha \approx 2\cdot10^{-3}$ suggests that these results are reproducible. Specimens cleaved from different areas of the same preform as well as from different preforms were used in these measurements. Of course the angle α permits estimation of the number of cusps oriented along only one of two perpendicular directions along the twinning planes (more precisely, their total number on the two twinning planes bounding the twin). However the consistent thickness of the twinning interlayer perpendicular to the axis of the preform together with the mechanical twinning technology used in this case make it likely that a single angle α is sufficient for an adequate description of TP defects. This is also confirmed by the comparatively narrow spread of the experimental points in Fig. 3.

The dashed lines in Fig. 3 represent an approximation of the measured relations by a polynomial of the type $y = x_0 + x^n$:

$$T_c(\alpha) = T_{c0} - (2.0\pm0.25)\cdot10^{-2} + A\alpha^{1/3\pm0.03},\ \mathrm{K},$$
$$T_b(\alpha) = T_{c0} - (5.0\pm0.50)\cdot10^{-2} + A\alpha^{1/3\pm0.05},\ \mathrm{K},$$

where A is a numerical coefficient equal to $\sim10^{-1}$ K.

The following are the most important results of those shown in Fig. 3: First there is no noticeable trend towards a variation in the difference of the critical temperatures of TPS T_c and T_b, which is equal to 0.03–0.04 K, and, second, T_c

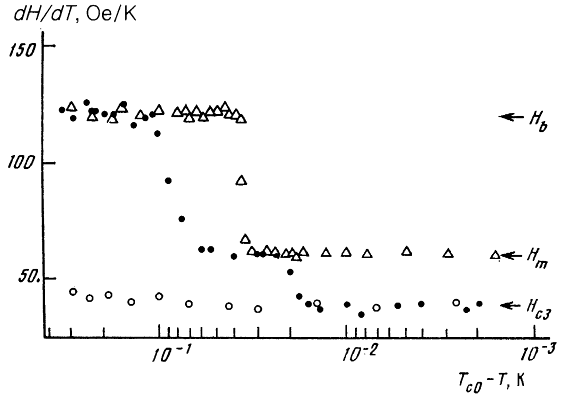

FIG. 2. Results of numerical differentiation of point-plotted temperature dependences of the supercooling field of the specimens: ○—single crystal, ●—$\alpha = 1.2\cdot10^{-4}$ rad, △—$\alpha = 1.4\cdot10^{-3}$ rad. Near T_{c0} the temperature of the specimens was determined based on measurements of the reference critical field $H(T)$. The arrows on the right represent the derivatives of the critical fields H_b, H_m, and H_{c3} determined in Fig. 1a.

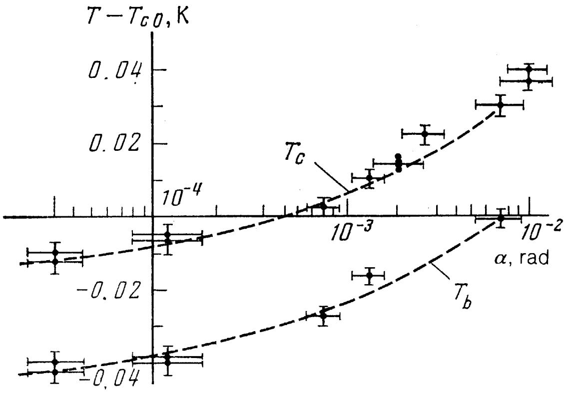

FIG. 3. Measurement results for the critical temperatures of TPS T_c and T_b plotted as a function of α; the dashed line represents the approximating power-law relations.

and T_b approach their final values as $\alpha \to 0$; according to these measurements such values lie somewhat below T_{c0}.

As we see from Fig. 3 the critical temperatures T_{c0} and T_c coincide at $\alpha = (5\text{–}6)\cdot 10^{-4}$. When a TP model consisting of atomically smooth sections separated by single-atom cusps is used, such an angle corresponds to distances of $\sim 6\cdot 10^3$ Å between the cusps, which is approximately twice the coherence length ξ_0 of superconductivity of monocrystalline tin, which is $\sim 3\cdot 10^3$ Å (Ref. 3). This estimate reveals that the experiments were carried out on specimens for which the distances between the defects were both much less than and much greater than ξ_0.

Specimens with angles α exceeding 10^{-2} were also fabricated and analyzed. Two-, three-, and four-moment jumps corresponding to the field H_m of the absolute instability of the normal TP state, were observed in the experimental dependences of the magnetic moment on the magnetic field in such specimens at $T > T_{c0}$. The values of each of the fields H_m measured for these specimens corresponded to several TPS critical temperatures T_c over the interval $T_{c0} < T_c < T_{c0} + 0.04$ K. Evidently this indicates that for $\alpha > 10^{-2}$ the twinning plane divides into individual sections with different, rather small (less than could be estimated based on the value of α in the homogeneous cusp distribution model) defect density. This phenomenon is rather well known for intercrystal boundaries and is called coring (see, for example, Refs. 7, 8). In coring the angle α ceases to be a characteristic of the structure of the intergrain boundary, at least in the sense that this parameter is used in the present study.

Finally, some comments regarding the observed metastable heated states and the anisotropy of the critical magnetic fields of TPS. As noted above, quantitative processing of measurements of the critical heating fields is impossible due to the uncertainty of the values of the magnetizing factor of these specimens. However, a comparison of the experimental curves for specimens containing twinning planes and single crystal control specimens of similar shape indicates that in the presence of TPS the region of metastable heated states is significant and is 2–3 times narrower. This indicates that normal phase nuclei enter the bulk of a specimen in the superconducting state from the direction of the twinning plane. Therefore the narrowing of the heating region represents one additional argument supporting the claim of Ref. 1 of spatial inhomogeneity of the superconducting state of TP.

The anisotropy of the critical magnetic fields of TPS was not systematically analyzed in the present study. All measurements were carried out for a near-parallel orientation of the TP and H. At the same time it should be pointed out that while the conclusions of previous studies regarding the virtual absence of anisotropy for such critical fields of TPS as H_d and H_m remain valid, it was discovered that anisotropy may be quite noticeable for the H_b field, on a level of 30–40% or higher. Precisely such a result could have been anticipated based on the previous treatment of $H_b(T)$ as a critical magnetic field separating the spatially homogeneous and inhomogeneous superconducting states of TP.

DISCUSSION OF RESULTS; CONCLUSIONS

The primary results of the present study is the identification of the role played by existing defects at the TP in the phenomenon of twinning plane superconductivity. The observed critical temperatures of TPS were found to depend on the number of defects at the TP. For example the critical temperature of TPS T_c in tin may lie both above and below the critical temperature of bulk superconductivity T_{c0}. However, all fundamental qualitative properties of the test phenomenon examined in Ref. 1 remain unchanged with any variations in defect density at the TP. Such qualitative characteristics of TPS should include the two critical temperatures T_b and T_c, the critical magnetic fields $H_b(T)$, $H_d(T)$, and $H_m(T)$ and such an important property of TPS as the spatial inhomogeneity of the superconducting state of TP for $H_b(T) < H < H_d(T)$.

The conclusion of the presence of spatial inhomogeneity in Ref. 1 was based on the following observations: First under these conditions the TP has a finite resistivity; second, the supercooling range of bulk superconductivity is substantially narrower; third, the possibility for bulk supercooling remains; fourth, anisotropy is very nearly entirely absent. Finally the present study has identified a reduction in size of the region of superheated superconducting states of the bulk of these specimens in the presence of TPS, which also indicates spatial inhomogeneity of the superconducting states of TP.

The dependence of the critical parameters of TPS on defect density at the TP makes it possible to uniformly describe the extensive variety of H, T-phase diagrams of supercooling in tin from Ref. 9 which have long remained without any explanation. We can reliably claim that the anomalies in the superconductivity properties of the tin specimens identified in Ref. 9 were due to the presence in these test specimens of twins characterized by different densities of defects localized at the twinning planes.

The measurements carried out in this study could then be used to estimate the critical parameters of TPS for the limiting case $\alpha = 0$. This case corresponds to a crystallographically-coherent, atomically-smooth TP in the model utilized. It was discovered that, in spite of the fact that both critical temperatures of TPS in this limiting case lie below the critical temperature of bulk superconductivity, the trend whereby they vanish is not observed and they remain near T_{c0}.

Therefore the present study has demonstrated that the causes of TPS as well as the various characteristic observed properties of TPS can be attributed to the physical properties that occur on the atomically smooth regions of the TP. The conclusion that spatially inhomogeneous states also exist on the atomically smooth regions of the TP is the least trivial conclusion. These are characterized solely by "short-range" order over lengths that are evidently less than ξ_0, in the absence of "long-range" order.[1] As discussed previously in Ref. 1 the "scenario" of the observed variations in TPS properties as a function of the magnetic field and temperature in all its essential qualitative properties is in precise agreement with the results from Ref. 10, although it is also necessary to cite other possible causes of the spatially inhomogeneous states of TPS. For example we cannot completely exclude the probability that spatial inhomogeneity analogous to the instability generating charge density waves in Ref. 11 arises in a two-dimensional superconducting TP system, or, that this same system contains some localized effects similar to those examined in Refs. 12, 13. It should be emphasized that with respect to the phenomenon of twinning plane superconductivity none of these or any other possible explanation for the onset of spatially inhomogeneous states has yet been theoretically analyzed, and the causes of such states in this case await an explanation.

One other important unresolved issue is the question of the effect of TP defects on the critical parameters of TPS. It is evidently not coincidental that T_c rises above T_{c0} only at distances between the defects on the TP below $\sim 2\xi_0$. Undoubtedly the interaction between the TP and its surrounding three-dimensional crystals plays a significant role in TPS. The magnetic field expulsion observed from the onset of diamagnetism originates from the rather thick layer surrounding the TP [1]. It is quite likely that underlying our result is the fact that ξ_0 is the characteristic correlation length of Cooper pairing in the crystal bulk.

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[1] I. N. Khlyustikov, Zh. Eksp. Teor. Fiz. **94**, (3) 311 (1988) [Sov. Phys. JETP **67**, 607 (1988)].
[2] I. N. Khlyustikov and M. S. Khaykin, Pis'ma v ZhETF **36**, 132 (1982) [JETP Lett. **36**, 164 (1982)].
[3] I. N. Khlyustikov and A. I. Buzdin, Adv. Phys. **36**, 271 (1987); Usp. Fiz. Nauk **155**, 47 (1988) [Sov. Phys. Usp. **31**, 409 (1988)].
[4] K. N. Tu and D. Turnbull, Acta Metallurgica **18**, 915 (1970).
[5] A. M. Kosevich and V. S. Boyko, Usp. Fiz. Nauk **104**, 201 (1971) [Sov. Phys. Uspekhi **14**, 286 (1971)].
[6] J. Feder and D. S. McLachlan, Phys. Rev. **177**, 763 (1969).
[7] A. N. Orlov, V. N. Perevezentsev, and V. V. Rybin, *Grain Boundaries in Metals.* Metallurgiya Press, Moscow, 1980.
[8] V. E. Fradkov and L. S. Shvindlerman, Poverkhnost', No. 9, 1 (1982).
[9] T. E. Faber, Proc. Roy. Soc. **241**, 531 (1957).
[10] S. Doniach and B. A. Huberman, Phys. Rev. Lett. **42**, 1169 (1979).
[11] J. A. Wilson, F. J. Di Salvo and S. Mahajan, Adv. Phys. **24**, 117 (1975).
[12] N. F. Mott and E. A. Davis, *Electronic Processes in Noncrystalline Matter*, Clarendon, Oxford (1979).
[13] L. N. Bulaevskiĭ and M. V. Sadovskiĭ, Zh. Eksp. Teor. Fiz. **92**, 672 (1987) [Sov. Phys. JETP **65**, 380 (1987)].

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