

Localized superconductivity of twin metal crystals

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The new phenomenon of twinning plane superconductivity is reviewed. It has already been observed in several metals. The superconductivity is localized near a twinning plane and it appears at a temperature higher than the critical temperature of the superconducting transition of a bulk metal. The phase diagram for the twinning-plane superconductivity, plotted using the magnetic field and temperature as the coordinates, is very different for type I and type II superconductors. A detailed analysis of the experimental data on the twinning-plane superconductivity is accompanied by a theoretical description of the phenomenon. The presence of a dense twinned structure may increase considerably the critical temperature: for example, in the case of tin it has been possible to increase this temperature more than threefold. We shall discuss also the data showing that the twinning-plane superconductivity can play an important role in the recently discovered high-temperature superconductors.

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I. INTRODUCTION

Superconductivity of a new object in the form of a twinning plane in metal crystals was discovered recently and investigated.¹⁻¹⁷ This twinning-plane superconductivity (TPS) has a number of unique properties which distinguish this phenomenon from the conventional bulk superconductivity. In addition, the physics of twins is attracting increasing interest (see, for example, Refs. 18–24).

By definition, twinning represents formation of two single-crystal regions (twins) with the crystal structures which are related by the point symmetry operation. The twinning plane is the boundary between these twins and it is one of the crystallographic planes.

We shall consider the simplest model example of a twin in a two-dimensional crystal lattice with a rectangular unit cell. Figure 1a shows a twin bicrystal and Fig. 1b illustrates, for the sake of comparison, a general boundary between grains. The twin boundary in Fig. 1a is a new mirror symmetry plane, but in general twinning may be associated with the appearance of a new C_2 symmetry axis and/or a new center of inversion (absent in the original single crystal). Twinning causes breakdown of the translational invariance at right-angles to the twinning plane, but—as demonstrated in Fig. 1a—the translational symmetry is retained in the direction

of the twinning plane. Atoms located on this plane have special positions compared with other atoms in a bicrystal and in turn they form a crystal of dimensionality which is a unity less than the original crystal. We can easily see that the boundary atoms in Fig. 1b do not form any crystal.

In the case of atoms lying on a twinning plane all the valence bonds are occupied, as in a single crystal, and in the first approximation the interatomic distances are conserved in all the coordination spheres. Moreover, all the atoms in this plane are located on continuations of crystal planes. Therefore, the distortions of the lattices of the two crystal-lites or grains forming a twin should be minimal and they should decrease rapidly away from the twinning plane. This is a major difference between a twinning plane and an ordinary plane boundary (Fig. 1b) where local stresses of the order of the Young modulus are inevitable. These circumstances are responsible for the exceptionally low energy associated with a twinning plane.

Twinning frequently occurs in the course of plastic deformation and twins are also formed as a result of crystal growth faults or because of annealing of cold-worked samples.²⁵⁻²⁷ The conditions under which twinning occurs during plastic deformation have been investigated in detail for tin.²⁷ A low excess energy of a twin boundary has the effect that annealing at temperatures close to the melting point

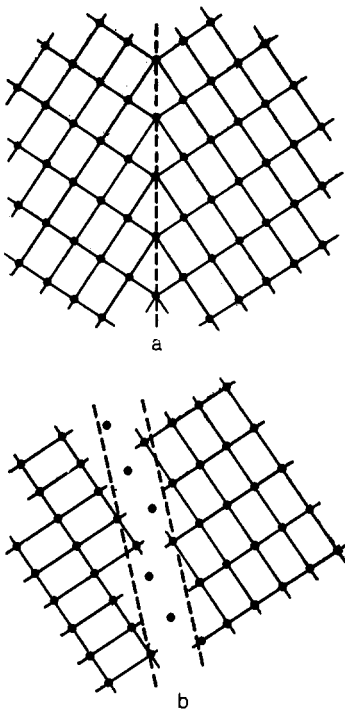


FIG. 1. a) Model of a twin in the simplest case of a two-dimensional crystal lattice with a rectangular unit cell. b) General boundary for the same crystal.

causes no changes in such a boundary, whereas the density of dislocations may decrease considerably. It is known from electron microscopic investigations that twinning may create atomically smooth parts of a boundary extending over distances of several microns.²¹⁻²³ The exceptionally low excess energy of a twinning plane is responsible also for the existence of twin structures in small particles even when these particles consist of just a few tens of atoms. Dislocations which distort a crystal lattice over relatively large distances have not yet been detected in particles of this size.²⁸

The presence of a twinning plane may give rise to a new branch of two-dimensional phonons and a two-dimensional group of electrons, which do not exist in a three-dimensional single crystal. In this case the twinning plane represents indeed a crystal not only as a set of points distributed regularly in space, but also as an actual physical two-dimensional object with its own atoms and quasiparticles. A study of the properties of such twinning-plane crystals is undoubtedly of interest, but it is a fairly difficult task. The main problem in investigations of this kind is obviously the extremely small number of atoms forming a twinning plane, compared with the number of atoms in the whole sample.

The study of twinning planes requires the development and use of special highly sensitive measurement methods and also, with the aim of increasing the amplitude of the recorded signals, of a technology of preparation of samples with a controlled but large number of twins. On the other hand, a twinning plane is a "perpetual" two-dimensional crystal: the three-dimensional crystals surrounding a twinning plane protect it from any damage or contamination.

At present the most promising approach is a study of many of the cooperative effects due to a twinning plane which have clear and strong manifestations, such as ferromagnetism or superconductivity. A ferromagnet has a large

spontaneous magnetic moment, whereas the resistance of a superconductor falls to zero and it exhibits a strong diamagnetism because of the Meissner effect.

A twinning plane is particularly interesting from the point of view of superconductivity, because the very special conditions needed for the Cooper pairing are more likely to be satisfied near a twinning plane than in the bulk. Consequently, the critical temperature of the transition of a twinning plane to the superconducting state may be higher than the transition temperature of the crystallites surrounding this plane. The following considerations suggest that this may be true: 1) when the condition of existence of two-dimensional phonons is satisfied, their velocity is found to be less than the velocity of bulk phonons; 2) the reticular density of atoms in the twinning plane in some of the crystal structures is less than in the bulk. These two circumstances indicate softening of the phonon spectrum in a twinning plane and a consequent increase in the electron-phonon interaction constant (see, for example, Refs. 29 and 30).

We cannot exclude the possibility of the appearance of new excitations specific to a twinning plane. For example, vibrations of atoms near a twinning plane should be strongly anharmonic because of the characteristic features of the potential relief. In this case the anomalously large amplitude of the vibrations of atoms at the boundary between twins tends to enhance the electron-phonon coupling.

We can identify immediately some specific difficulties which are encountered in experimental studies of the TPS. The first is the proximity effect,^{31,32} because of which the critical temperature T_c of the superconductivity transition of an isolated twinning plane should be slightly higher than T_{c0} , which is the critical temperature in the bulk (therefore, in particular, the TPS is unlikely to occur in macroscopic nonsuperconducting metal crystals). Secondly, at temperatures below T_{c0} it is difficult to investigate the TPS because of the screening by the superconducting bulk.

It is well known that the width of the transition to the superconducting state is considerably greater for plastically deformed samples than for single crystals of the same material and that plastic deformation creates regions in a sample with a higher transition temperature.³³ The width of the transition in a perfect single crystal is less than 1 mK, whereas in the case of deformed samples it may reach 1 K (Ref. 34). Usually the appearance of regions with a higher transition temperature in plastically deformed samples is explained by the fact that the transition temperature of the majority of superconductors depends on the external pressure. In fact, near defects in a crystal (such as dislocations) there are stress fields which can be regarded as an excess pressure. Numerical estimates of the pressure ensuring the experimentally observed shift of the temperature of the transition to the superconducting state gives values of the order of one-tenth of the Young modulus of a given material, which in most cases is of the same order of magnitude as the yield stress (see, for example, Ref. 35).

Creation of dislocations is not the only mechanism of plastic deformation. In some cases, for example at low temperatures and high deformation rates, plastic deformation may be due to the formation of twins.²⁷ As pointed out already, the stresses near twins are low so that they are not regarded as a possible cause of the broadening of the superconductor transition. Nevertheless, an investigation of the

structure of the intermediate state carried out many years ago³⁶ indicated that a twinning plane may influence the superconducting properties of samples.

The question arises what are the crystal defects which can increase most effectively the transition temperature T_{c0} . We can attempt to answer this question by investigating the superconducting properties of samples with low and controlled concentrations of defects of a specific type. Clearly, such investigations would be subject to very stringent requirements in respect of the sensitivity of the measurement methods.

The published investigations¹⁻¹⁰ mentioned below demonstrate that twins have a considerable influence on the temperature of the transition to the superconducting state. We can expect this mechanism of increase in T_{c0} to be very common and it is twins rather than dislocations that are largely responsible for the observed broadening of the transition in deformed samples, although investigations of the influence of the internal pressure in a crystal on T_{c0} would also be of major interest.

In the present review we shall consider all the experimental data on the superconductivity of a twinning plane and also provide a theoretical description of the localized superconductivity applicable to this case. Our attention will be concentrated on the characteristics of an isolated twinning plane, the behavior of the TPS in a magnetic field, the difference between the TPS of type I and II superconductors, and observation of a topological phase transition.⁷ We shall discuss the problems of interaction of closely spaced twinning planes and also the TPS of small particles, which suppresses the proximity effect and enhances considerably (in the case of tin by a factor of 2-3)⁵ the critical temperature. Some of the topics not considered in the present review for lack of space (for example the critical current of the TPS and the behavior of the critical fields at low temperatures) are discussed in Ref. 73.

2. PROPERTIES OF SAMPLES

The majority of the experimental investigations of the TPS considered below were carried out using a magnetometric method. A detailed description of a SQUID magnetometer with a magnetic flux sensitivity of 10^{-9} G·cm² can be found in Refs. 37-39.

In magnetometric investigations of the superconductivity the results of measurements represent a two-dimensional surface in the coordinate space (H, T, M) i.e., in the space of

a magnetic field, temperature, and magnetic moment of a sample. The required surface can be constructed almost completely by investigating its sections in a constant magnetic field or at a constant temperature.

The investigations of the TPS had been made on samples of seven metals. The main parameters, needed in the subsequent discussion, are listed in Table I. This table gives the crystal structures of metals and orientations of twinning planes in them. The purity of the investigated metals, represented by the ratio $\rho_{300K}/\rho_{4.2K}$, is also included in Table I. Samples were grown from low-melting-point metals by methods which made it possible to obtain single crystals characterized by $\rho_{300K}/\rho_{4.2K} \sim 10^5$ and by mean free paths of electrons up to several millimeters.^{40,41}

Crystal defects formed as a result of plastic deformation can be investigated using bicrystals. It is generally accepted that low-angle grain boundaries consist of dislocations. Bicrystals with a large misorientation angle between the grains (crystallites) make it possible to investigate more complex structures which distinguish real samples from ideal single crystals. Measurements of the misorientation angles between the two components of a bicrystal and also of the angles between the plane of the boundary and the crystallographic axes make it possible to estimate the density and nature of dislocations forming the boundary and determine whether this boundary is of a special type, particularly if it is a twin boundary. In the experiments discussed below, investigations were made of bicrystals of metals, including twins, formed as a result of growing a sample from two seeds oriented with the aid of the Laue diffraction patterns to within 1-3° [Sn, Nb (Refs. 42 and 43), and In] and also as a result of annealing of a strongly cold-worked sample at temperatures close to (up to ~0.1 K) to the melting point listed in Table I (Al, Pb, In, Sn). A study was also made of mechanical twins formed at liquid nitrogen temperature (Sn, In, Tl) and at room temperature (Sn, Re). All the mechanical twins were kept at 24 h at room temperature and a considerable proportion of the mechanical twins of tin was also subjected to annealing at temperatures close to the melting point.

The methods used in the preparation of the samples could not guarantee the absence of defects in a twinning plane. Moreover, an estimate of the precision of the orientation of the seeds indicated that the distances between grain-boundary dislocations could be of the order of hundreds of interatomic spacings. The same distance between grain-boundary dislocations were obtained also for mechanical twins using measurements of the dimensions of a twin wedge

TABLE I. Properties of investigated metals.

| | Crystal structure | Twinning plane | $\rho_{300K}/\rho_{4.2K}$ | $T_m, ^\circ\text{C}$ | T_{c0}, K | H_{c0}, Oe | $dH_c/dT _{T_{c0}}, \text{Oe/K}$ | $dH_{c2}/dT _{T_{c0}}, \text{Oe/K}$ | $\xi_0, \text{\AA}$ | κ |
|-------|-------------------|----------------|---------------------------|-----------------------|--------------------|---------------------|----------------------------------|-------------------------------------|---------------------|----------|
| 1. Sn | tetr. | (304) | $\sim 10^5$ | 231,9 | 3,722 | 308 | -165 | -30 | 3100 | 0,13 |
| 2. In | tetr. | (101) | $\sim 10^5$ | 156,6 | 3,4145 | 289 | -169 | -14 | 3600 | 0,06 |
| 3. Nb | bcc | (112) | $\sim 5 \cdot 10^2$ | 2487 | 9,3 | | | | | 1 |
| 4. Re | hex. | (1012) | $\sim 10^3$ | 3180 | 1,698 | 198 | -233 | -490 | 400 | |
| 5. Tl | hex. | (1012) | $\sim 5 \cdot 10^3$ | 303,5 | 2,38 | 179,5 | -151 | | 4000 | |
| 6. Al | fcc | (111) | $\sim 10^4$ | 660,1 | 1,1796 | 104,9 | -178 | -3,5 | 12000 | 0,014 |
| 7. Pb | fcc | (111) | $\sim 10^3$ | 327,3 | 7,1999 | 803,4 | -223 | -189 | 800 | 0,6 |

along and across the direction of a twinning plane (in the case of the investigated samples the ratio of the dimensions of the twinning wedge was $\sim 10^2$). Samples of the required dimensions and shape were cut from bicrystal blanks using spark machining. The surface layer damaged in the process of cutting was then etched away in a solution suitable for a given metal.

It should be pointed out that in an investigation of the influence of defects of the crystal lattice of materials on their low-temperature properties carried out using bicrystals it is necessary to ensure equality of the thermal expansion coefficients of the crystallites forming a twinning boundary. In the case of anisotropic substances, which include tin, if the thermal expansion coefficients are not matched, then cooling to helium temperatures can create new uncontrolled defects. By way of record, it should be mentioned that the thermal expansion coefficients of tin differ approximately twofold when measured along and across the fourfold symmetry axis.

The next columns of Table I give the critical temperatures T_{c0} of the transitions of metal single crystals to the superconducting state, the critical magnetic fields H_{c0} at $T = 0$, and the slopes of the dH_c/dT curves at $T = T_{c0}$. Such values can be used conveniently as the reference temperatures and also in calibration of the magnetometer.

The last two columns of Table I give the values of the parameters $dH_{c2}/dT|_{T_{c0}}$, ξ_0 , and κ of the investigated materials.

3. SUPERCONDUCTIVITY OF AN ISOLATED TWINNING PLANE. EXPERIMENTS

3.1. Twinning-plane superconductivity of a type I superconductor (tin)

The discovery of the TPS was the result of an experimental investigation of diamagnetism of plastically deformed samples. Typical dependences of the magnetic moment of a deformed sample of tin (which is a type I superconductor) are plotted in Fig. 2. The dependences ob-

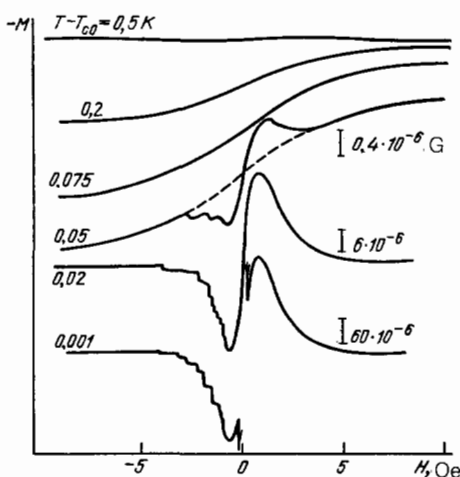


FIG. 2. Magnetic-field dependences of the magnetic moment of a sample of tin at various temperatures.³⁷ The two uppermost curves exhibit a fluctuation diamagnetic moment, whereas the lowest three curves exhibit diamagnetism of a twinning plane (M_d). A discontinuity of the lowest curve is due to the appearance of bulk superconductivity in the sample. The field was varied from left to right.

tained at temperatures in the range $T - T_{c0} \geq 0.07$ K exhibit clearly a fluctuation of a diamagnetic moment M_f , investigated in detail in, for example, Ref. 44. At temperatures $T - T_{c0} \leq 0.05$ K, in addition to the fluctuation diamagnetism, there should be also an additional diamagnetic moment M_d which appears only in the case of a plastically deformed sample and the amplitude M_d rises proportionally to the degree of plastic deformation.³⁷ A discontinuity of the experimental dependence near $H = 0$ at $T - T_{c0} = -0.001$ K is due to the appearance of bulk superconductivity in a sample.

When the absolute value of the magnetic field is increasing, the dependence $M_d(H, T)$ can be described within experimental error by the following empirical relationship

$$M_d(H, T) \propto H \exp\left(-\frac{H}{H_0}\right) \exp\left(-\frac{T}{T_0}\right), \quad (3.1)$$

where $H_0 \approx 0.8$ Oe is the magnetic field corresponding to the maximum value of M_d and $T_0 \approx 0.01$ K is the characteristic temperature scale.

Investigations⁴⁴⁻⁴⁷ of the fluctuation diamagnetism of superconductors above the critical temperature have also revealed exponential temperature dependences of the diamagnetic moment similar to that described by Eq. (3.1). These dependences do not fit the concept of fluctuation diamagnetism, but the question of the origin of this effect has not been discussed.⁴⁵⁻⁴⁷ Consequently, the relationship between the diamagnetic moment M_d and the plastic deformation of samples has for a long time been unexplained.

A reduction in the magnetic field H from a high value (≥ 10 Oe) results in discontinuities of the moment in the dependences $M_d(H)$, but these are not observed when the field is rising. Since changes in the magnetic moment of a sample are extremely rapid, we can nevertheless measure quite accurately the magnetic fields H_m (discontinuity fields) for each of the observed abrupt changes in the moment. Cooling shifts the whole system of discontinuities toward higher fields and the slope of the dependence $H_m(T)$ is the same for all the discontinuities. The numerical value of the slope is

$$\frac{dH_m}{dT} \approx -35 \text{ Oe/K.}$$

Each discontinuity of the magnetic moment may be attributed to the appearance of superconductivity (at a temperature above T_{c0}) in a small volume of a sample near a certain group of crystal defects. The identity of the slopes dH_m/dT for all the discontinuities of the magnetic moment indicates that the increase in the critical temperature can only be due to crystal structure defects of one type. Amplitudes of the discontinuities of the magnetic moments and the fields at which they are observed can, in principle, provide information on the actual characteristics of defects of this type.

Experiments carried out on bicrystals showed that an increase in the critical transition temperature of tin to the superconducting state deduced from the appearance of the diamagnetic moment M_d is observed only in the presence of twins in a sample. Figure 3 shows schematically the arrangement used and the results obtained in one of the experiments. In these experiments a detection coil of short length (~ 1.5 mm) was used and it was found that the displacement of a

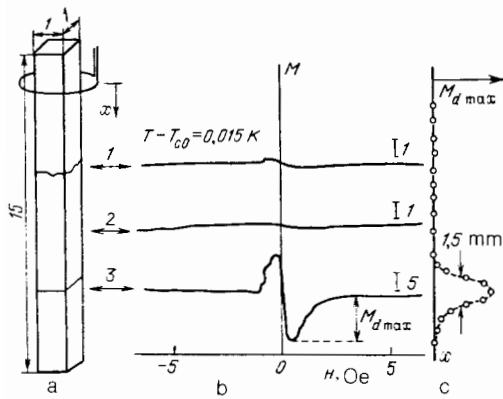


FIG. 3. Schematic diagram of the experimental arrangement and the results obtained in a study of different sections of a sample of tin composed of three crystallites (all dimensions are in millimeters). a) Schematic diagram: 1) general boundary; 2) single-crystal region; 3) twinning plane. b) Experimental dependences $M_d(H)$. c) Coordinate dependence of the maximum value of the diamagnetic moment M

long sample relative to the coil made it possible (as demonstrated on the left-hand side of the figure) to investigate various parts with the coordinate resolution of ~ 2 mm. A sample consisted of three crystallites formed as a result of crystallization during annealing of a blank subjected to a preliminary strong plastic deformation. One of the crystallite boundaries (lower one in the figure) was a twinning plane, and the other had a crystallographic orientation differing by ~ 15 – 20° from that of the twinning plane. The middle part of the figure shows examples of experimental dependences of the magnetic moment of different parts of a sample on the magnetic field. The dependences shown in Fig. 3b were obtained for the single-crystal part of a sample and they exhibited only the fluctuation diamagnetism. The part of the sample containing the boundary other than the twinning plane had a diamagnetic moment M_d of amplitude comparable with the fluctuation moment (curve 1). The third record (3) representing the part of the sample with a twinning plane indicated that the diamagnetic moment M_d in fields below 1 Oe exceeded almost 100-fold the fluctuation diamagnetism. Finally, the right-hand side of Fig. 3 shows the dependence of the amplitude of the diamagnetic moment M_d on the coordinate along a sample. The results of this experiment demonstrated clearly that the observed increase in the critical superconducting temperature was due to a twinning plane and not due to fields of internal crystal stresses (known to be considerably higher near the upper boundary in Fig. 3, which was not the twinning plane).

It is worth describing specially a control experiment in which a sample was subjected to plastic deformation at an elevated ($\sim 150^\circ\text{C}$) temperature. This temperature was far too low to cause recrystallization of tin and plastic deformation occurred entirely due to creation of dislocations.²⁷ The absence of a characteristic "crackling" sound (tin cry) during plastic deformation was evidence that twins did not form. This sample did not exhibit the diamagnetic moment M_d .

The superconductivity associated with the twinning plane was confirmed also in experiments in which measurements were made of the impedance of an rf circuit containing a crystal of tin.³ Figure 4 shows an example of the experi-

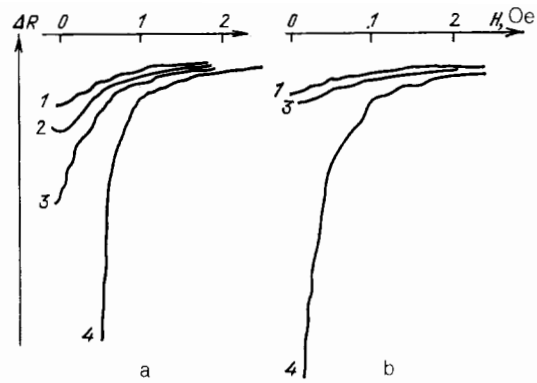


FIG. 4. Dependence of the resistance of a sample of tin on the magnetic field at different temperatures.³ $T - T_{c0}$ (K): 1) 0.02; 2) 0.01; 3) 0.005; 4) 0.001.

mentally recorded resistance (real part of the impedance) of a sample of $10 \times 4 \times 4$ mm dimensions as a function of the applied magnetic field. A twinning plane was perpendicular to the long axis of the sample and was located closer to one of its edges. An rf-circuit coil was 2 mm long. The records shown in Fig. 4a were obtained when the coil enclosed a part of a sample with the twinning plane, whereas that in Fig. 4b was recorded for a control single-crystal part of the same sample. The presence of the twinning plane reduced considerably the resistance in weak fields at temperatures $T > T_{c0}$.

For some of the sample containing a twinning plane the dependences of the magnetic moment on the magnetic field were much simpler than those shown in Fig. 4. A distinguishing feature of such samples (which exhibited only one discontinuity) was that the trace of a twinning plane emerging on the outer surface of a sample was absolutely straight. This straightness of the trace of the twinning plane on the surface of a bicrystal was checked with an optical microscope with a resolution down to $\sim 1 \mu\text{m}$. Samples with a "bent" twinning plane always had dependences $M_d(H)$ with a large number of jumps. Bending of the crystalline boundary was known to correspond to different densities of grain-boundary dislocations in different parts of the twinning plane, but the quantitative relationship between the nature and density of grain-boundary dislocations in a twinning plane and the characteristics of the dependences $M_d(H, T)$ have not yet been established, although it clearly exists.

Using the value of the diamagnetic moment M_d and assuming that the magnetic susceptibility of a superconducting layer near a twinning plane is $-1/4\pi$, we can estimate the effective volume of this layer. Later, using the fact that the area of a twinning plane is known (from the dimensions of the sample and that there is only one twinning plane) and assuming that the superconducting layer is continuous, we can find the "effective thickness" w of the layer. The temperature dependence of the magnetic moment M_d means that the thickness of the superconducting layer w increases as a result of cooling. Typical values of the effective thickness w in zero magnetic field, found by extrapolation of the experimental dependences to $T = T_c$ and $T = T_{c0}$, are respectively $\sim 10a$ (a is the interatomic distance) and $\sim \xi_0$ (the definition of T_c as the critical temperature of the TPS will be given later).

3.2. Phase diagram of the twinning-plane superconductivity of tin

We shall now draw attention to the asymmetry of the dependences $M_d(H)$ relative to the point $H = 0$ (Figs. 2 and 3). The experimental records obtained on reduction in the absolute value of the magnetic field caused the diamagnetic moment M_d to appear abruptly in a field H_m . An increase in the magnetic field (in either direction from zero) failed to reveal any singularities such as discontinuities or kinks in the dependences $M_d(H)$. More detailed investigations indicated that the appearance of a discontinuity of the moment M_d in a field H_m requires the application of a magnetic field exceeding a certain critical value H_d . In the opposite case the dependences $M_d(H)$ are identical for rising and falling fields (they become reversible) and there are no singularities. The inset in Fig. 5 identifies by the arrow a the dependence of the diamagnetic moment M_d in the case when the initial magnetic field exceeds H_d , whereas the arrow b shows the dependence in the opposite case. The value of the moment M_d in a field H_d in these samples was found to be considerably lower than the magnetometer noise level. For this reason the above method for the determination of H_d , used in Refs. 4 and 6, is the only one possible.

In magnetic fields between H_d and H_m a twinning plane in tin can be in one of two different states characterized by the presence or absence of the diamagnetic moment M_d . This is clear evidence that the transition of the twinning plane in tin to the superconducting state is a first-order phase transition and is accompanied by a clear supercooling effect. In this range of magnetic fields the long-lived metastable state is that in which the twinning plane has no magnetic moment and this state is attained on reduction of the field from fairly high values, whereas the field H_m corresponds to the absolute instability of the normal state of the twinning plane. Most probably the field H_d corresponds to a thermodynamic equilibrium between the normal and superconducting states of the twinning plane. The absence of metastable states on destruction of the TPS by a magnetic field is ex-

plained by the fact that far from a twinning plane there is always metal in the normal state which acts as a nucleus of the normal phase⁴ in the TPS.

As in the case of the dependences $H_m(T)$, the slope of the dependences $H_d(T)$ is the same for all the investigated samples: $dH_d/dT \approx -125$ Oe/K. The straight lines $H_m(T)$ and $H_d(T)$ intersect the axis and one another at the same point (within experimental error) and this is the point T_c corresponding to the critical temperature of the TPS. In the direct vicinity of T_c the diamagnetic moment M_d is very small and the critical temperature T_c was obtained in Ref. 4 only by extrapolation of the dependences $H_m(T)$ and $H_d(T)$.

It therefore follows that it is possible to determine experimentally the following parameters of each sample: T_{c0} is the critical temperature of the bulk superconductivity, $H_c(T)$ is the critical magnetic field of the bulk superconductivity, T_c is the critical temperature of the TPS, $H_d(T)$ is the thermodynamic-equilibrium critical magnetic field of the TPS, $H_m(T)$ is the field of the absolute instability of the normal state of a twinning plane, T_0 is the characteristic temperature for the dependence $M_d(T)$ [Eq. (3.1)], and H_0 is the characteristic magnetic field for the dependence $M_d(H)$ [Eq. (3.1)].

In those cases when the dependences $M_d(H)$ exhibit small jumps of the magnetic moment, each jump has its own set of the above parameters.

The ranges of the magnetic fields and temperatures in which these parameters were obtained for twins in tin are fairly wide. For example, in the case of the parameter T_0 we found values ranging from ~ 0.023 to ~ 0.0006 K.

Nevertheless, all the twin bicrystals of tin (their total number was of the order of 100) prepared by the methods discussed in Sec. 2 satisfy the following relationships:

$$\begin{aligned} T_{c0} &= 3.722 \text{ K (reference temperature),} \\ \left. \frac{dH_c}{dT} \right|_{T_{c0}} &= -165 \text{ Oe/K (reference slope),} \\ T_c - T_{c0} &= 4T_0, \\ \frac{dH_d}{dT} &\approx -125 \text{ Oe/K,} \\ \frac{dH_m}{dT} &\approx -35 \text{ Oe/K,} \\ \frac{H_0}{T_0} &\approx 120 \text{ Oe/K,} \\ w|_{T_{c0}, H=0} &\approx 3500 \text{ \AA.} \end{aligned} \quad (3.2)$$

Since the conditions of Eq. (3.2) are satisfied, we can use the normalized coordinates and plot a universal (H, T) phase diagram of the TPS of tin shown in Figs. 5 and 6 and describing the behavior of all the samples in a magnetic field.

Figure 5 shows a part of the phase diagram of the TPS of tin at temperatures exceeding T_{c0} . Temperature is measured from the reference point which is the critical temperature of the bulk superconductivity T_{c0} . Normalization of the axes increases to T_0 and H_0 [see Eq. (3.1)].

The (H, T) phase diagram of Fig. 5 shows the results of measurements of the dependences $H_c(T)$, $H_d(T)$, and $H_m(T)$. The lines $H_c(T)$, $H_d(T)$, and $H_m(T)$ split the (H, T) phase plane into four regions. Region I [below the $H_c(T)$ line] corresponds to the bulk superconductivity; region II [above the $H_d(T)$ line] is the normal state; regions III and IV are the regions where the twinning-plane superconductivity is observed. A metastable normal state can exist in region III.

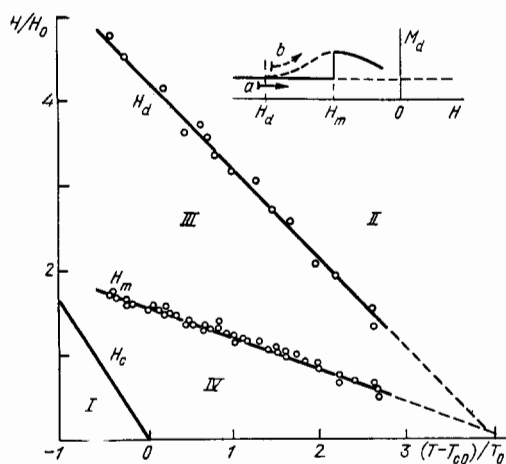


FIG. 5. (H, T) phase diagram of the twinning-plane superconductivity of tin.⁴ The axes are normalized as described in text. The inset shows a part of an experimental record of $M_d(H)$. Region I in the phase diagram corresponds to bulk superconductivity; II is the normal state; III and IV are the regions where the twinning-plane superconductivity is observed. A metastable normal state can exist in region III.

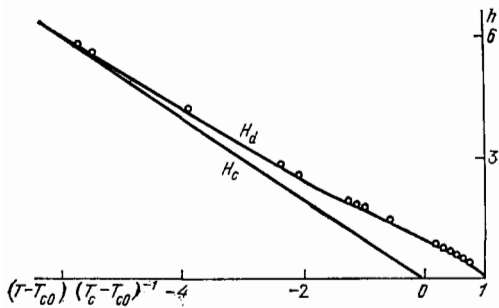


FIG. 6. Phase diagram throughout the investigated range of temperatures obtained for the twinning-plane superconductivity of tin. The symbols are the experimental values taken from Ref. 6 and the $H_d(T)$ curves are theoretical; here, $h = H[(T_c - T_{c0})(dH_c/dT)_{T_c - T_{c0}}]^{-1}$.

IV [between the $H_c(T)$ and $H_d(T)$ lines] are the regions of existence of the TPS and in region III [above the line $H_m(T)$] the twinning plane may be in a metastable normal state.

The (H, T) phase diagram in Fig. 6 is plotted using the following coordinates: $(T - T_{c0})/(T_c - T_{c0})$ along the temperature axis and $H[(dH_c/dT)_{T_c - T_{c0}}(T_c - T_{c0})]^{-1}$ along the magnetic field axis.

This phase diagram includes the line denoted by $H_c(T)$ which intersects the temperature axis (in the selected coordinates) at the point 0. The second line is $H_d(T)$ which intersects the temperature axis at T_c . The circles in Fig. 6 are the results of experimental measurements and the line is theoretical (its calculation will be discussed in the next section). It is worth noting the existence of a lower temperature limit T_{c2} for the observation of the TPS. This is the temperature at which the $H_c(T)$ and $H_d(T)$ curves intersect. The existence of the bulk superconductivity prevents the observation of the TPS in the case of the dependences of the magnetic moment of the samples on the magnetic field at a fixed temperature. The value of T_{c2} for tin is

$$T_{c2} - T_{c0} = -6.5 (T_c - T_{c0}). \quad (3.3)$$

The existence of the temperature T_{c2} is not self-evident; in principle, the $H_d(T)$ curve could pass just above $H_c(T)$ without intersecting the latter anywhere and this could be true right down to zero temperature. The existence of T_{c2} is a consequence of the fact that tin is a type I superconductor (for details see Sec. 4.2.3).

In the case of samples with an isolated twinning plane the magnetic field was expelled from a relatively thin (with an effective thickness $w \approx 3.5 \times 10^{-5}$ cm at $T = T_{c0}$) layer surrounding a twinning plane. The dimensions of the twinning plane were ~ 1 mm. Had the superconducting layer surrounding the twinning plane been continuous, such a relationship between the geometric parameters of the layer would have led (because of the change in the demagnetization factor) to an anisotropy of the properties of the TPS when the mutual orientation of the twinning plane and the magnetic field were altered. These experimental investigations demonstrated that the behavior of the TPS of tin throughout the investigated range of magnetic fields and temperatures depended little on the orientation of the twinning plane and the magnetic field so that the anisotropy of the field H_m did not exceed 30%. Detailed investigations of

the anisotropy of the TPS had not yet been carried out.

One should also point out that, as demonstrated by the magnetic measurements reported in Ref. 4, that the electrical resistance of an isolated twinning plane in tin was always finite.

The absence of anisotropy and the finite electrical resistance indicated that a single coherent superconducting state did not appear near an isolated twinning plane and that the magnetic field was expelled only from microscopic regions.

3.3. Twinning-plane superconductivity of a type II superconductor (niobium)

The examples of the dependences of the magnetic moment of niobium bicrystals on the magnetic field are plotted in Fig. 7 for three temperatures close to T_{c0} of niobium. The continuous curves are the results of measurements on a twin and the dashed curves are the measurements on a control single crystal. The relatively small diamagnetic moment, depending nonlinearly on the magnetic field, of the control sample was due to the usual three-dimensional fluctuations of the superconductivity. Clearly, the sample containing a twinning plane exhibited a much stronger (compared with the control sample) diamagnetism which was similar to the diamagnetism M_d of tin in respect of the magnetic-field and temperature dependences. The general features of the dependences of the magnetic moment M_d on the magnetic field applied to tin (Figs. 2 and 3) and niobium (upper curve in Fig. 7) twins are clear and do not need detailed comments. Therefore, we shall draw attention to the differences between the dependences $M_d(H)$ observed for niobium and tin twins.

The magnetic moment M_d of niobium varies always reversibly and smoothly with the magnetic field and there is no overheating or supercooling (compare Fig. 7 with Figs. 2, 3, and 5). This behavior of $M_d(H)$ suggests that the transition to the TPS state in niobium is of the second order. The absence of jumps of the magnetic moment in the dependences

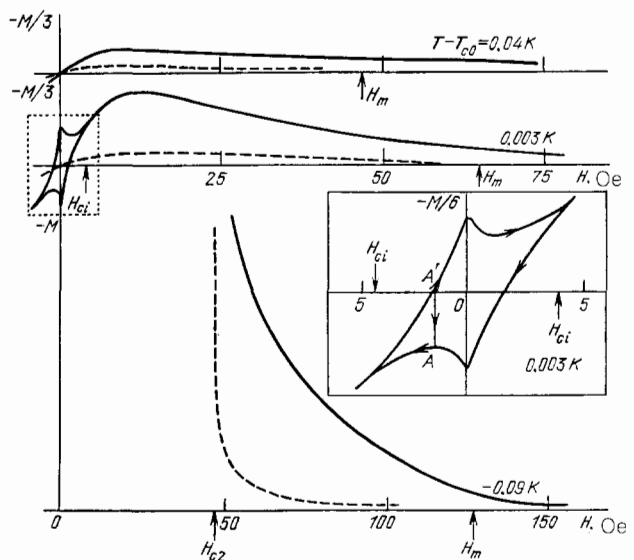


FIG. 7. Dependence of the diamagnetic moment (in relative units) of a niobium twin on the magnetic field applied at various temperatures. The dashed curves are the results of measurements on control samples which did not have a twinning plane.

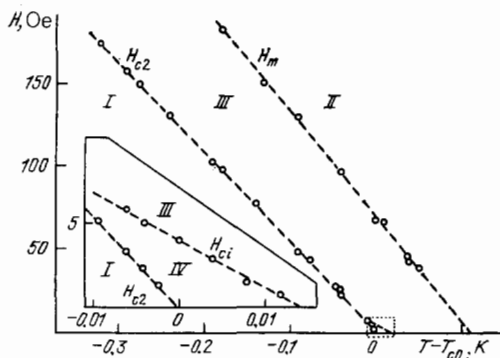


FIG. 8. Phase diagram of the twinning-plane superconductivity of niobium in a tilted field.⁷ Region I is the bulk superconductivity, II is the normal state, III and IV represent the twinning-plane superconductivity. Zero resistance is observed in region IV. A part of the phase diagram shown enlarged in the inset is identified by a dotted rectangle near the abscissa.

$M_d(H)$ means that a different criterion of the magnetic field H_m of the TPS has to be used. In Ref. 7 the field H_m is arbitrarily taken to be the field in which the diamagnetic moment M_d is 10 times higher than the magnetometer noise level. This criterion of H_m gives only a lower limit of the range of existence of the TPS in niobium. The dependence of the magnetic moment of the magnetic field at temperatures below T_{c0} is shown in the lower part of Fig. 7, which demonstrates that there should be no difficulty in determining experimentally the upper critical field H_{c2} of niobium.

Figure 8 shows the temperature dependences of the critical magnetic field. This phase diagram includes lines in the upper critical magnetic field of the bulk superconductivity H_{c2} and the critical field of the TPS H_m . These lines divide the (H, T) phase diagram into three regions: I [which is the region lying below the $H_{ci}(T)$ line] representing the bulk superconductivity; II [above the $H_m(T)$ line] which is the region of the normal state, and III and IV taken together [between the $H_{c2}(T)$ and $H_m(T)$ lines] are the regions of observation of the TPS of niobium.

The considerable differences between the behavior of the magnetic-field dependences of the moment $M_d(H)$ of niobium and the behavior of $M_d(H)$ in the case of tin is demonstrated by the curve in the center of Fig. 7 corresponding to the temperature $T - T_{c0} = 0.003$ K. In weak magnetic fields (this part of the curve is shown on a larger scale in the inset on the right) there is a hysteresis which disappears in a field H_{ci} . Such a hysteresis loop is typical of the magnetic-field dependences of the magnetic moment of a thin superconducting disk subjected to a magnetic field tilted relative to its plane.^{48,49} The magnetic moment of the disk can correspond to any point in the (M, H) plane inside the hysteresis loop. This indeterminacy of the moment is governed by the superconducting current flowing along the macroscopic circuit representing the periphery of the disk. The limit cycle of the hysteresis loop corresponds to the excitation in this loop of the maximum possible critical current I_c corresponding to a given external magnetic field H .

We checked that the current producing the magnetic-moment hysteresis flowed along a twinning plane by measuring the moment in the same sample for two orientations

of this plane relative to the magnetic field. In the first case the field was approximately perpendicular to the twinning plane. This gave the experimental results shown in Fig. 7. In the second case the magnetic field was again not parallel to the twinning plane, but now the angle between this plane and the field was ~ 10 – 15° . The magnetic moment of the current flowing along the macroscopic loop was then five times less and this agreed with the reduction in the coefficient of the coupling between the loop or circuit formed by the periphery of the twinning plane and the detection coil of a superconducting magnetic flux transducer. The hysteresis-free moment M_d was practically unaffected and there was no change in the critical magnetic fields H_{ci} , H_m , and H_{c2} .

The line $H_{ci}(T)$ is also plotted in the (H, T) phase diagram of Fig. 8 and on a larger scale in the inset in this figure. The $H_{ci}(T)$ line intersects the temperature axis at the point T_{ci} and divides the region of existence of the TPS of niobium into two parts: III [region lying below the $H_{ci}(T)$ line] which is characterized by the fact that there are no nondecaying currents flowing along macroscopic circuits (nondecaying currents flow only along microscopic singly connected regions) and there is no hysteresis; IV [below the $H_{ci}(T)$ line] is the region where in addition to the diamagnetic moment M_d there is a hysteresis, i.e., the magnetic flux may be trapped because of the appearance of nondecaying currents flowing along circuits of macroscopic dimensions. In other words, the topology of the nondecaying currents changes on the $H_{ci}(T)$ line.

When the current excited in a macroscopic circuit is less than the critical value (and the state of the superconducting system is represented by a point inside the hysteresis loop), small changes in the external magnetic field are screened completely because of a change in the value of the circuit current. Under these conditions the differential magnetic susceptibility dM/dH (with the slope of the line AA' in the inset in Fig. 7) can be used, for a known orientation of the superconducting circuit relative to the magnetic field (for example, the orientation may be mutually perpendicular), to estimate the area of the loop or contour along which nondecaying electric currents flow. In the experiments under discussion this area is the same as the area of the twinning plane. Therefore, knowing the area of the loop we can use the magnetic moment to estimate quite readily the critical current I_c .

The critical temperatures T_c and T_{ci} of the investigated niobium twins were determined by extrapolation of the experimental dependences $H_m(T)$ and $H_{ci}(T)$ to the point of intersection with the temperature axis (by analogy with the determination of T_c of tin twins). Exactly as in the case of tin, the magnetic moment M_d was used to estimate the "effective" thickness w of the superconducting layer near a twinning plane. An estimate of the critical current density j_c was obtained assuming that a tube of a nondecaying current I_c had a cross-sectional area $\sim w^2$.

In the case of niobium the magnetic field H_0 corresponding to the maximum magnetic moment M_d did not remain constant, but decreased on increase in temperature. The value of H_0 tended to zero at temperatures T approaching T_c .

We shall now summarize the main characteristics of the TPS in niobium deduced from the magnetic measurements:

$$\begin{aligned}
T_{c0} &= 9.4 \text{ K (reference temperature),} \\
\left(\frac{dH_{c2}}{dT}\right)_{T=T_{c0}} &= -490 \text{ Oe/K (reference slope),} \\
T_c - T_{c0} &= 0.11 \text{ K} \approx 4T_0, \\
T_{ci} - T_{c0} &= 0.016 \text{ K,} \\
\frac{dH_m}{dT} &= -560 \text{ Oe/K,} \\
\frac{dH_{ci}}{dT} &= -270 \text{ Oe/K,} \\
w|_{T=T_{c0}, H=0} &\approx 400 \text{ \AA} \approx \xi_0, \\
j_c|_{T=T_{c0}, H=0} &\approx 10^7 \text{ A/cm}^2, \\
\frac{dH_0}{dT} &= -130 \text{ Oe/K.}
\end{aligned} \tag{3.4}$$

It follows from the magnetic measurements that in region IV (in the phase diagram of Fig. 8) we can expect a macroscopic superconducting current, i.e., the resistance of a twinning plane measured between two distant points becomes zero. This makes it possible to investigate the TPS below T_c using the method of currents.

An attempt to carry out such investigations on niobium twins was reported in Ref. 7. The magnetic-field dependences of the critical superconducting current along a twinning plane were determined at a constant temperature. The apparatus used in this investigation made it possible to carry out measurements at temperatures from ~ 2.5 to ~ 8 K in magnetic fields up to ~ 4 kOe. The upper critical magnetic field H_{c2} of niobium was deduced from the characteristic steep fall of the critical current on increase in the magnetic field. In the range $H > H_{c2}$ the investigated samples exhibited a small (~ 0.3 A) critical current of the surface superconductivity. In this case the external magnetic field was oriented exactly parallel to the twinning plane and it was found that above H_{c3} the critical current observed for twinned samples was considerably higher than the critical current for the surface superconductivity and this was true right up to the field $H_m^* > H_{c2}$. When the direction of the external field was tilted away from the twinning plane by an angle of $\sim 1^\circ$ the critical current in the fields $H_{c2} < H < H_m^*$ became equal to the critical surface superconductivity current. Such an increase in the critical current was not observed⁷ for control samples in which the two component crystallites were not separated by a twinning plane.

When the $H_m^*(T)$ line was plotted using the (H, T) coordinates, its slope was found to be $dH_m^*/dT = -550$ Oe/K and at 4.2 K was approximately 300 Oe higher than the H_{c2} line.

Unfortunately, the relatively high conductivity of niobium samples in the normal state and the low critical currents prevented measurements by the method of currents⁷ at temperatures exceeding ~ 8.5 K, i.e., in the region where the magnetometric investigations were carried out. The absence of data on the critical field $H_m^*(T)$ at temperatures in excess of ~ 8.5 K did not allow us to determine sufficiently accurately, on the basis of the measured currents, the critical temperature of the TPS, but clearly this temperature should be identical with T_{ci} .

We shall now consider in greater detail the main differences between the phase diagram of the TPS in niobium (Fig. 8) and the phase diagram of the TPS in tin (Figs. 5 and 6). Firstly, the transition of niobium to the TPS is most probably a second-order phase transition. Secondly, there is

no lower temperature limit to the observation of the TPS. Throughout the investigated range of temperatures, at least from ~ 2.5 to ~ 9.5 K, the $H_m(T)$ and $H_m^*(T)$ lines do not intersect the $H_{c2}(T)$ line anywhere. In Sec. 4.2 these observations are attributed to the difference between the values of κ for tin and niobium. Thirdly, the phase diagram of Fig. 8 shows a line of a topological phase transition $H_{ci}(T)$. The existence of phase transitions in two-dimensional systems in which there is a change in the nature of the correlation functions of the order parameter suggests a change in the topology of nondecaying electric currents in a superconductor, predicted in earlier theoretical treatments.^{50,51} Another theoretical investigation is reported in Ref. 52 and it is based on a model of a thin superconducting film in vacuum; an attempt is made to construct the phase diagram of this system. According to Ref. 52, the transition of a film to the superconducting state is due to cooling in two stages at temperatures denoted in Ref. 52 by T_{BCS} and T_{KT} . Initially, a state with a strong diamagnetism appears at a temperature identified as T_{BCS} ; the resistance measured between two distant points on the film differs from zero. Further cooling gives rise to a topological phase transition at the Kosterlitz-Thouless temperature T_{KT} and the resistance of the film vanishes. The identical qualitative features of the behavior of the dependences $M(H, T)$ in niobium twins and of the results reported in Ref. 52 suggest that the line $H_{ci}(T)$ and the temperature T_{ci} are, respectively, the line and the critical temperature of the topological phase transition of the Berezinskii-Kosterlitz-Thouless type. In the investigated part of the (H, T) plane, located above the $H_c(T)$ line, there is no topological phase transition in tin twins. Fourthly, an investigation of tin twins failed to reveal characteristics of the samples dependent strongly on the mutual orientation of the twinning plane and the magnetic field. In the case of niobium when a magnetic field is tilted relative to the twinning plane it is possible to observe zero electrical resistance of this plane only in magnetic field exceeding ~ 7 Oe [region IV below the $H_{ci}(T)$ line in Fig. 8]. In the case of a magnetic field parallel to the twinning plane a region of zero resistance of the twinning plane to the electric current becomes much wider. This is clearly due to the fact that the components of the magnetic field normal and tangential to the twinning plane have different effects on the TPS. Only the normal component of the field creates vortices in the superconducting layer and the resistance of the twinning plane becomes different from zero in a magnetic field higher than H_{ci} . However, in the case of parallel orientation of the twinning plane and the magnetic field the vortices do not appear and the $H_m^*(T)$ line is close, within the limits of the experimental error, to the $H_m(T)$ line.

3.4. Other metals. Conclusions

In addition to the results of investigations of the TPS in tin and niobium described in detail above, measurements had been made on twins in indium, rhenium, thallium, aluminum, and lead. A diamagnetic moment M_d was observed, as in the case of tin and niobium, above the temperatures T_c in the case of indium, rhenium, and thallium. However, in the case of aluminum and lead only the diamagnetism due to bulk fluctuations of the superconducting phase was observed at temperatures above T_{c0} . By way of example, Fig. 9

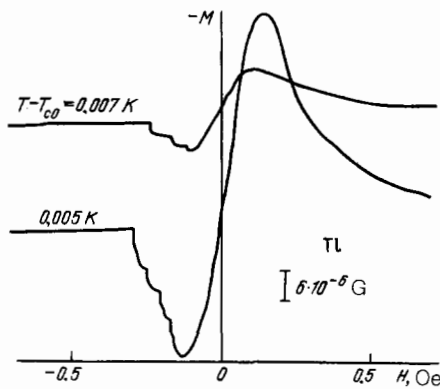


FIG. 9. Magnetic-field dependences of the diamagnetic moment of the twinning-plane superconductivity of thallium recorded at different temperatures.

shows the experimental dependences of the magnetic moment of a thallium twin on the magnetic field recorded at two different temperatures. Clearly, these dependences are fully analogous to the dependences $M_d(H)$ reported for tin twins (Fig. 2).

The values of the parameters of the TPS may lie within a fairly wide range, as demonstrated in the case of tin in Sec. 4.2; nevertheless, we can speak of certain average values which are those most frequently encountered. In the case of the investigated metals they are given in Table II. It should be stressed that the data in this table were obtained for samples annealed at temperatures close to the melting point (see Sec. 2). In studies of the samples deformed at helium temperatures (see, for example, Refs. 8–10, 53 and 54) it was reported that the critical temperatures of the transition to the superconducting state increased considerably; it was pointed out that annealing of the samples again reduced the critical temperature. The authors of these papers attributed the increase in the critical temperatures to twinning, but the increase reported by them was mainly due to defects of a twinning plane characterized by a large excess energy (this was why they were annealed). This confirmed the idea put forward in Sec. 3.2 that twinning plane defects can affect the critical temperature of this plane considerably.

TABLE II. Characteristics of the twinning-plane superconductivity of metals.

| | $\Delta T_c = T_c - T_{c0}, K$ | T_0, K | H_0, Oe |
|-------|--------------------------------|----------|-----------|
| 1. Sn | 0.04 | 0.01 | 0.8 |
| 2. In | 0.01 | 0.001 | 0.1 |
| 3. Nb | 0.11 | 0.3 | 10 |
| 5. Re | 0.006 | 0.0015 | 0.5 |
| 5. Tl | 0.003 | 0.0008 | 0.1 |
| 6. Al | 0 | — | — |
| 8. Pb | 0 | — | — |

It is clear from Table II that the TPS is a very common phenomenon. At temperatures above the critical temperature of the bulk transition to the superconducting state T_{c0} it has been possible to observe the TPS for five out of seven investigated metals, since only two of them do not exhibit the TPS. It is interesting to note that a common feature of the metals exhibiting the TPS (which distinguishes them from the metals that do not exhibit this phenomenon) is that twinning occurs along crystallographic planes in which the reticular density of atoms is less than the volume density. In the case of aluminum and lead with the fcc lattice the twinning process occurs along a close-packed plane. The lower density of atoms in a twinning plane may tend to soften the phonon spectrum of this plane, as pointed out in the Introduction.¹⁾

It is clear from Table II that tin and niobium are characterized by the largest difference $T_c - T_{c0}$, which is approximately an order of magnitude higher than the value for the other metals. The relatively wide range of temperatures of observation of the TPS has been responsible for the fact that the most detailed investigations had been carried out on tin and niobium.

The presence of a twinning plane in samples of indium, niobium, tin, rhenium, and thallium enhances the superconducting properties of these metals. The critical temperature of the transition to the TPS state T_c is higher than the bulk critical temperature T_{c0} . Moreover, the critical magnetic field of the TPS (at least in a certain range of temperatures) exceeds the critical magnetic field H_c (H_{c2} for niobium). The transition to the TPS state may be a first-order phase transition (indium, tin, rhenium, thallium) or a second-order transition (niobium).

It was reported recently that the presence of twinning planes in organic superconductor β -(ET)₂I₃ enhances its superconducting properties⁹²: when multiple twinning occurs, the critical temperature rises from 8 to 9 K.

4. THEORETICAL DESCRIPTION OF THE TWINNING-PLANE SUPERCONDUCTIVITY

4.1. Modified Ginzburg-Landau functional

Experimental investigations demonstrate that in the temperature range $T_c > T > T_{c0}$ the superconductivity appears only in a thin layer near a twinning plane. In this case an important role is played by the proximity effect in a superconductor and a normal (at temperatures $T > T_{c0}$) metal. Consequently, the critical temperature of the TPS is only slightly higher than T_{c0} , i.e., $\tau_0 = (T_c - T_{c0})/T_{c0} \ll 1$.

This makes it possible to describe the TPS near T_{c0} by the Ginzburg-Landau functional (see, for example, Ref. 55), but this should allow for enhancement of the superconductivity near a twinning plane. The mechanism of this enhancement is not yet clear. We pointed out above that enhancement of the Cooper pairing near a twinning plane may be due to the specific nature of this plane as a two-dimensional crystal: the plane has a new soft two-dimensional phonon mode, the electron spectrum of the twinning plane has special features, the Coulomb repulsion is weakened, and the twinning plane may have defects. It is important to note that, although because of the proximity effect the value of T_c is only slightly higher than T_{c0} , a change in the Cooper pairing constant near a twinning plane compared with its bulk value

is quite considerable. This is supported by a report⁵ of a strong (severalfold) increase in the critical temperature of small tin particles containing a twinning plane because the proximity effect in such particles is suppressed (see Sec. 5).

The problem of the mechanism of enhancement of the Cooper pairing near a twinning plane is naturally very interesting. However, the region where the Cooper pairing is enhanced extends from a twinning plane to distances not exceeding several (or several tens) of the interatomic spacings. This is much less than the superconducting correlation length ξ_0 and from the point of view of the Ginzburg-Landau functional (which describes the behavior of the superconducting order parameter at distances greater than ξ_0) such a distance is only δ -like. Therefore, in describing the TPS we should supplement the Ginzburg-Landau functional with the δ -function term $-\gamma\delta(x)|\psi(r)|^2$, which allows for the enhancement of the Cooper pairing near a twinning plane. Here, the twinning plane corresponds to $x = 0$ and $\psi(r)$ is a complex superconducting order parameter. It should be stressed that the nature of the functional is very general and it is not related to any specific mechanism of enhancement of the superconductivity at a twinning plane, which determines the actual value of the constant γ .²³

It therefore follows that the modified Ginzburg-Landau functional for the description of the TPS is

$$F = \int \left[\frac{(\mathbf{B}-\mathbf{H})^2}{8\pi} + \frac{1}{4m} \left| \left(\nabla - \frac{2ie}{c} \mathbf{A} \right) \psi \right|^2 + a |\psi|^2 + \frac{b}{2} |\psi|^4 - \gamma\delta(x) |\psi|^2 \right] dr, \quad (4.1)$$

where the following notation⁵⁵ is used: $a = \tau/\eta$, $b = 1/N\eta$, $\tau = (T - T_{c0})/T_{c0}$, \mathbf{H} is the external field, $\mathbf{B} = \text{curl } \mathbf{A}$ is the magnetic induction, N is the electron density, and $\eta = 7\xi(3)E_F/6(\pi T_{c0})^2$ in the case of a pure superconductor and $\eta = 1.42lE_F/v_F T_{c0}$ in the case of a dirty semiconductor (l is the mean free path of electrons). All the coefficients in the above functional, with the exception of γ , represent the bulk superconductivity and are quite familiar. The only unknown parameter needed in the description of the TPS is the quantity γ which is related directly to $\tau_0 = (T_c - T_{c0})/T_{c0}$, i.e., it is related to the critical temperature of the TPS (see below). If we substitute the experimental value of τ_0 , we are dealing with the function (4.1) in which all the coefficients are known and which, in principle, should provide a *full* description of the TPS near the temperature T_{c0} .

A theory of the TPS based on the modified Ginzburg-Landau functional is developed in Refs. 6, 11, 12, and 16 and we shall give a detailed account of this theory. We shall begin by noting that in the case of a type I superconductor (such as tin) this theory can account completely for the full range of existence of the TPS (Refs. 6 and 16). In the case of type II semiconductors it is valid near the temperature T_{c0} ; at low temperatures the critical field for the TPS is found by solving a complete integral equation for Ψ (Refs. 14 and 16), but the modified Ginzburg-Landau functional still provides a qualitatively correct description of the TPS throughout the full temperature range.

In the absence of a magnetic field the superconducting order parameter Ψ depends only on the coordinate x , which represents the distance from a twinning plane, and the equation for $\psi(x)$ obtained from the functional of Eq. (4.1) is

$$\left(\frac{1}{4m} \frac{\partial^2}{\partial x^2} - \frac{\tau}{\eta} \right) \psi - b |\psi|^2 \psi = -\gamma\delta(x) \psi. \quad (4.2)$$

We can find the temperature T_c of the appearance of the localized superconductivity by restricting Eq. (4.2) to terms linear in respect of ψ :

$$\frac{1}{4m} \frac{d^2\psi}{dx^2} - \frac{\tau}{\eta} \psi = -\gamma\delta(x) \psi. \quad (4.3)$$

The solution of Eq. (4.3) which increases in the limit $x \rightarrow \pm \infty$ is

$$\psi(x) \propto \exp(-q|x|),$$

where

$$q^2 = 4\tau m/\eta.$$

The presence of the δ function on the right-hand side of Eq. (4.3) is equivalent to the following boundary conditions which ψ must satisfy at $x = 0$:

$$\psi'(0) = -2m\gamma\psi(0),$$

which yields

$$q = 2m\gamma,$$

so that the critical temperature of the TPS is related to the parameter γ by the expression

$$\frac{T_c - T_{c0}}{T_{c0}} = \tau_0 = m\eta\gamma^2. \quad (4.4)$$

Equation (4.2) for the determination of the localized superconductivity temperature is an analog to the Schrödinger equation. Hence, it follows (see, for example, Ref. 56) that in the case of a filamentary region where the Cooper pairing is enhanced the excess of the critical temperature of the localized superconductivity above the value of T_{c0} is exponentially small. One can hardly hope for detection of the localized superconductivity near a thin (of thickness less than ξ_0) line defect. In the case of a point defect the localized superconductivity effect is altogether absent (this essentially corresponds to the case when there is no bound state in a shallow three-dimensional potential well⁵⁶), but in this case the localized superconductivity may appear at the few clusters of point defects.^{57,58} It should be pointed out that the localized superconductivity appears in a magnetic field also at isolated point defects.⁵⁹

The value of τ_0 is a characteristic temperature scale for the description of the TPS. It follows from Eq. (4.2) that the characteristic length scale is then

$$\xi(\tau_0) = \left(\frac{\eta}{4m\tau_0} \right)^{1/2},$$

whereas the order parameter is

$$\psi_0 = \left(\frac{\tau_0}{\eta b} \right)^{1/2}.$$

We shall find it convenient to introduce dimensionless reduced variables: the temperature $t = (T_c - T)/(T_c - T_{c0})$, the coordinate $x' = x/\xi(\tau_0)$ and the order parameter $\varphi = \psi/\psi_0$. Equation (4.2) then becomes

$$-\frac{d^2\varphi}{dx'^2} + t\varphi + \varphi^3 = 2\delta(x) \varphi. \quad (4.5)$$

In future we shall omit the prime on the dimensionless coordinate x' . Equation (4.5) admits a first integral and we can readily obtain its exact solution:

$$\varphi(x) = \frac{(2t)^{1/2}}{\operatorname{sh}(|x|t^{1/2} + p)}, \quad p = \frac{1}{2} \ln \frac{1+t^{1/2}}{1-t^{1/2}}. \quad (4.6)$$

When temperature is lowered $1 > t > 0$ the amplitude of the order parameter increases and the region around a twinning plane where the superconductivity is localized becomes wider. The temperature $t = 0$ corresponding to the appearance of bulk superconductivity is characterized by a change in the law governing the fall in the localized superconductivity amplitude with distance from the twinning plane: at $t = 0$ the exponential law is replaced by the power law $\varphi(x) \propto x^{-1}$ (which is a characteristic critical effect). Below the temperature of the bulk transition to the superconducting state T_{c0} the order parameter $\psi(x)$ has its local maximum at a twinning plane and the corresponding solution of Eq. (4.2) is readily obtained in quadratures. A discontinuity of the specific heat due to the appearance of the superconductivity localized at a twinning plane amounts to $\Delta C = 2\xi(\tau_0)/\eta^2 b T_{c0}$ (per unit area).

The only unknown parameter of our theory τ_0 [or γ ; see Eq. (4.4)] can be calculated in the TPS model which assumes that the dimensionless Cooper pairing constant $\lambda = \lambda_0 + \delta\lambda(x)$ has a sharp maximum near a twinning plane.

We shall not discuss the details of the calculation, which is based on solution of the integral equation for the superconducting order parameter,^{11,13} but give only an order-of-magnitude estimate $\tau_0 = (T_c - T_{c0})/T_{c0}$. This estimate is readily obtained from the following considerations: the localized superconductivity is a region near a twinning plane and the size of this region is of the order of the superconductivity correlation length at $T = T_c$, given by $\xi(T_c) \propto \xi_0 \tau_0^{-1/2}$, where $\xi_0 = 0.18 v_F/T_{c0}$ [$\xi^2(\tau) = 0.55 \xi_0^2/\tau$] and if the peak of λ is concentrated in a region of width $d \ll \xi_0 \ll \xi(T_c)$ near a twinning plane, the effective increase in λ amounts to $T_c \propto \omega_D \exp(-1/\lambda)$. Since $\delta\lambda d/\xi(T_c)$, it follows that

$$\frac{\delta T_c}{T_c} \propto \tau_0 \propto \left(\frac{\delta\lambda}{\lambda_0}\right)^2 \frac{d}{\xi(T_c)},$$

so that finally, after allowance for the temperature dependence of ξ , we obtain the following estimate

$$\tau_0 \propto \left(\frac{\delta\lambda}{\lambda_0} \frac{d}{\xi_0}\right)^2.$$

In the case of a dirty superconductor ($l \ll \xi_0$) the reduction in the correlation length increases the estimate τ_0 by a factor $(\xi_0/l) \gg 1$.

This model relates the TPS to the enhancement of the Cooper pairing near a twinning plane and the superconductivity is then due to bulk electrons. As pointed out before, the presence of a twinning plane should give rise also to localized electron states near this plane and these should be similar to the Tamm levels. Such surface electron superconductivity has properties quite different from the bulk effect⁶⁰ and, in particular, its critical temperature T_c can be higher. However, a twinning plane is located inside the bulk of a metal and an important role is played by the interaction with three-dimensional electrons, which spreads the superconductivity

deeper into the metal. Such a model of the localized superconductivity was considered in Ref. 17 and in this case the similarity of the critical temperatures T_c and T_{c0} for the TPS deduced on the basis of the above model can be explained only by a very strong interaction between "two-dimensional" and "three-dimensional" electrons. In the vicinity of the temperature T_c the description of the superconductivity due to three-dimensional electrons is provided by a model¹⁷ which also reduces to the modified Ginzburg-Landau functional of Eq. (4.1).

4.2. Phase diagram and magnetic properties of a twinning-plane superconductor

It follows from the experimental results given in Sec. 3 that the behavior of the TPS in a magnetic field is very special and the properties of the TPS differ in many respects from those of the conventional bulk superconductivity. The modified Ginzburg-Landau function of Eq. (4.1) provides, in principle, a complete description of the superconductivity localized near a plane (twinning plane in our case) in the vicinity of the temperature T_c . This description is largely universal and for a suitable selection of the dimensionless variables it is independent of the only unknown theoretical parameter which is the constant γ (if necessary, we can assume that this parameter is known from the experimental results).

We shall now consider the case of a magnetic field parallel to a twinning plane such that the vector potential A can be selected in the $A = A_y(x)$ gauge. Adopting dimensionless variables φ and x [see Eq. (4.5)] and also the vector potential $\tilde{A} = A/A_0$, where $A_0 = (\tau_0 mc^2/2\eta e^2)^{1/2}$, we shall write down the equations for the order parameter and the field distribution which follow from the functional of Eq. (4.1):

$$-\varphi'' + \frac{\varphi}{2} \tilde{A}^2 + t\varphi + \varphi^3 = 0, \quad \varphi'|_{x=+0} = -\varphi(0), \quad (4.7)$$

$$\tilde{A}'' = \frac{\varphi^2}{\kappa^2} \tilde{A}, \quad \tilde{A}(x \rightarrow \infty) = \frac{hx}{\kappa}. \quad (4.8)$$

Here, $\kappa = \lambda/\xi = (mc/e)(b/2\pi)^{1/2}$ is the Ginzburg-Landau parameter, h is the external magnetic field H normalized to $H_c(-\tau_0) = (2\tau_0/\eta)(\pi/b)^{1/2}$, $H_c(-\tau_0)$ is the thermodynamic critical field of the bulk superconductivity in the temperature interval $T_{c0} - (t_c - T_{c0})$, which determines the scale of the field in the case of the TPS exhibited by a type I superconductor. If $|x| \rightarrow \infty$ the external field H is identical with the magnetic induction B . Equations (4.7) and (4.8) represent essentially the usual Ginzburg-Landau equations⁵⁵ supplemented by the boundary condition which applies to φ at $x = 0$.

The nonlinear system of equations (4.7)–(4.8) gives, in principle, a complete description of the TPS in a parallel field. The first integral of the system (4.7)–(4.8) can be found easily (see, for example, Ref. 55) and in our case it can be written in the form

$$-2(\varphi')^2 + (2t + \tilde{A}^2)\varphi^2 + \varphi^4 - (\tilde{A}')^2 \kappa^2 + h^2 = 0. \quad (4.9)$$

An analytic investigation of the problem of the critical field of the TPS transition can be carried out only for type II superconductors or in the limiting case of type I superconductors characterized by $\kappa \ll 1$. If $\kappa \lesssim 1$, we have to solve the complete system of equations (4.7)–(4.8) on a computer (see Sec. 4.2.3).

4.2.1. Screening of a weak parallel field

The TPS exists in the temperature range $T_{c0} < T < T_c$ right down to the lowest fields and in this case we can pose the problem of the diamagnetic susceptibility of the TPS [corresponding to the initial slope of the dependence $M_d(H)$].

Screening of a weak magnetic field $\mathbf{B} \parallel \mathbf{z}$ parallel to a twinning plane is governed by Eq. (4.8), where instead of $\varphi(x)$ we must substitute the function describing the distribution of the order parameter in the absence of the field [see Eq. (4.6)]:

$$\tilde{A}'' - \frac{2t}{\kappa^2 \operatorname{sh}^2(|x|t^{1/2} + p)} \tilde{A}, \quad p = \frac{1}{2} \ln \frac{1+t^{1/2}}{1-t^{1/2}}. \quad (4.10)$$

Substituting a new variable $u = \coth(|x|t^{1/2} + p)$ and transforming Eq. (4.10) for the vector potential to an equation for the field B , we find that the distribution of the magnetic induction is described by

$$(u^2 - 1) \frac{d^2 B}{du^2} = -\frac{2}{\kappa^2} B \quad (4.11)$$

subject to the boundary conditions $B(u=1) = H$ (because far from a twinning plane the magnetic induction is equal to the external field) and $B'(u = \coth p) = 0$ (because the distribution of the magnetic induction is symmetric relative to the twinning plane and in the plane itself the value of B is minimal).

In the case of superconductors which exhibit the extreme type II behavior ($\kappa \gg 1$) the screening of the field is weak practically throughout the full temperature range $0 < t < 1$, i.e., the localized superconductivity hardly changes the field $B(x) = H - b(x)$, where $b(x) \ll H$. In the first approximation with respect to a small parameter $\kappa^{-2} \ll 1$, Eq. (4.11) can be written in the form

$$\frac{d^2 B}{dx^2} = -\frac{2H}{\kappa^2 (u^2 - 1)}, \quad (4.12)$$

which has an exact solution. Solving Eq. (4.12), we find that the magnetic field on the twinning plane itself is¹⁶

$$B(x=0) = H \left(1 - \frac{2}{\kappa^2} \ln \frac{t^{-1/2} + 1}{2} \right) \quad (4.13)$$

and it differs little from the external field H . Near the transition temperature T_c ($1 - t \ll 1$) the field distribution is given by

$$B(x) = H \left[1 - \frac{1-t}{2\kappa^2} (2x+1) \exp(-2x) \right]. \quad (4.14)$$

Knowing the field distribution, we can now find the total magnetic moment of the TPS per unit area:

$$M_d = \int_{-\infty}^{\infty} \frac{B(x) - H}{4\pi} dx = -H \frac{(1-t)}{4\pi\kappa^2} \xi(\tau_0) \quad \text{for } 1-t \ll 1. \quad (4.15)$$

Cooling enhances the screening and in the limit $T \rightarrow T_{c0}$ the magnetic moment¹⁶ becomes

$$M_d = -\frac{H \xi(\tau_0)}{\kappa^2 t^{1/2}} \cdot \frac{\pi}{6}, \quad (4.16)$$

which shows that the diamagnetic susceptibility considered in the limit $t \rightarrow 0$ diverges as $t^{-1/2}$. In the case of type II superconductors characterized by $\kappa \gg 1$ the condition of va-

lidity of Eqs. (4.12)–(4.16) is $t \gg \exp(-\kappa^2)$, i.e., these equations are valid throughout the full temperature range $0 < t < 1$.

This analysis applies also to type I superconductors near the critical temperature T_c in a temperature interval $1 - t \ll \kappa^2$. The physical meaning of this last condition is simple: the dimensionless effective screening length $\tilde{\lambda}_L^{-1} \propto \varphi(0)/\kappa \propto (1-t)^{1/2}/\kappa$ should be greater than the superconducting correlation length (which for our choice of the units of length is of the order of unity). The field then penetrates almost completely the whole superconducting region and the TPS behaves in fact as a type II superconductor.

In the other limiting case of $1 - t \gg \kappa^2$ the TPS of a type I superconductor can now screen the field quite strongly so that it becomes practically zero in a layer of thickness $|x| \gg 1$ near a twinning plane. The effective screening thus occurs at distances $x \gg 1$, i.e., in Eq. (4.11) we are interested in the range $u - 1 \ll 1$. Solving this equation in this range, we find¹⁶ that the magnetic field at a twinning plane is exponentially small and the magnetic moment per unit area is

$$M_d = -\frac{H}{2\pi} \xi(\tau_0) \left(\ln \frac{2}{\kappa} \right) t^{-1/2}.$$

It follows from the above expression that in a type I superconductor the magnetic field is expelled almost completely from the localized superconductivity region near a twinning plane, the size of which is $\sim \xi(\tau_0) t^{-1/2}$, i.e., it is of the order of the superconducting correlation length.

In comparing the expressions obtained for the diamagnetic susceptibility of the TPS with the experimental data for tin and niobium (Sec. 3), we note that the latter are one or one-and-a-half orders of magnitude lower than the theoretical estimate. Clearly, this circumstance is due to an inhomogeneity of a real twinning plane which consists of regular parts of different dimensions separated by regions with dislocations. This is probably the reason also for the exponential nature of the temperature dependence of the magnetic moment $M_d(T)$ (see Sec. 3.1).

In fact, the critical temperature of the appearance of the localized superconductivity near a part of a twinning plane (we are considering here a part of the plane where the Cooper pairing is enhanced) depends strongly on the size of such a region¹²: $\tau(R)$ rapidly approaches zero for parts of a twinning plane of $R < \xi(\tau_0)$ size. If the distribution of the sizes of such parts of a twinning plane is characterized by an average size smaller than $\xi(\tau_0)$, then the increase in the magnetic moment as a result of cooling is mainly due to an increase in the number of parts of the twinning plane that have become superconducting. An analysis of one of the simplest models of the distribution of superconducting parts of a twinning plane in accordance with their size is given in Ref. 12 and it indeed yields an exponential temperature dependence of the magnetic moment. Although the inhomogeneous nature of the twinning plane can explain qualitatively the steep fall of the magnetic moment of the TPS on increase in temperature, a quantitative comparison with the experimental results is not yet possible because the size distribution of superconducting parts of a twinning plane is not yet known.

Although the inhomogeneity of a twinning plane has a very strong influence on the dependence $M_d(H, T)$, we can nevertheless compare directly the experimentally determined (H, T) phase diagram with the theoretical predic-

tions of the fields $H_d(T)$ and $H_m(T)$ for the superconductivity extending over an infinite twinning plane. In fact, in the case of a type II superconductor the transition to the TPS state is of the second kind and, as the magnetic field is reduced, large (characterized by the maximum value of T_c) parts of a twinning plane are the first to become superconducting and this is followed by smaller parts (with lower values of T_c). In the case of the large parts [the characteristic size of which is large compared with $\xi(\tau_0)$] the critical field is practically equal to the critical field for an infinite plane.

In a type I superconductor (tin) the transition in the presence of a field is of the first order in the experimentally observable range of existence of the TPS. In this case a superconducting nucleus is activated by overcoming an energy barrier and "supercooling" of the normal phase is observed. This normal phase is retained in the applied field until superconducting nuclei become capable of growing, when the field reaches the value H_m corresponding to a field for a second-order transition. It should be pointed out that this supercooling field is H_m for an infinite twinning plane (corresponding to the maximum value of T_c), which is the highest value of H_m achieved for large parts of a twinning plane. The magnetic moment changes abruptly in the field H_m because many parts of the twinning plane go over abruptly to the TPS state.

An increase of the external magnetic field from zero causes a gradual suppression of the TPS beginning from small parts of a twinning plane. These transitions are of the first order until the field reaches the value $H_d(R)$. As pointed out in Sec. 3.2, overheating of the TPS is not observed because of the presence of a passive metal in the normal state near a twinning plane. The structure of the TPS in a field (applied exactly parallel to the twinning plane) should result in an abrupt change of the magnetic moment, but because only a small part of the twinning plane goes over to the normal state in this field, the resultant $M_d(H)$ curve should be smooth. Such a smooth dependence $M_d(H)$ may appear also because the field is inclined relative to a twinning plane (intermediate state). Vanishing of the magnetic moment indicates that the field has reached the value $H_d(R = \infty)$, i.e., that the conductivity is destroyed in all parts of the twinning plane. The field $H_d(R = \infty)$ defined in this way can be compared with the theoretical value for an infinite twinning plane.

An inhomogeneity of the twinning plane is also related to the question of a transition of the Berezinskii-Kosterlitz-Thouless type for the TPS, which arises in connection with the experimental observations of macroscopic currents at a certain Kosterlitz-Thouless temperature T_{KT} (lying between T_{c0} and T_c); this is discussed in Sec. 2.3. Since the TPS occurs in a region $\sim \xi(\tau_0)$ near a twinning plane, it cannot be regarded as two-dimensional. The London penetration depth λ_L near T_c is described by the relationship $\lambda_L^2 \sim \lambda_L^2(0) T_c / (T_c - T)$, in the TPS case, whereas the correlation length is described by $\xi^2 \propto \xi^2(\tau_0) \propto \xi_0^2 T_c / (T_c - T_{c0})$. Hence, we can readily see that the TPS is quasitwo-dimensional at temperatures $(T_c - T)/T_c < [\lambda_L(0)/\xi_0]^2 (T_c - T_{c0})$ (Ref. 61) and an estimate of the Kosterlitz-Thouless transition temperature T_{KT} at which the spontaneous creation of vortices takes place gives⁵²

$(T_c - T_{KT})/T_c \propto (T_c/E_F)^2 \ll 1$. The transition temperature T_{KT} is practically identical with the critical temperature of the TPS so that this transition can hardly be observed experimentally.

An inhomogeneity of the twinning plane may give rise to an alternative possibility of the Kosterlitz-Thouless transition, which occurs in a system of superconducting granules on a two-dimensional twinning plane. In fact, a weak Josephson interaction of the individual superconducting regions (for which the phase of the superconducting order parameter is constant) makes an inhomogeneous TPS similar to the classical system of planar rotators for which in fact the Kosterlitz-Thouless transition was predicted.^{50,51} The temperature of this transition T_{KT} is then of the order of the energy of the Josephson interaction of neighboring superconducting regions. In this sense the properties of an inhomogeneous TPS may be similar to the properties of planar Josephson structures.⁶²

4.2.2. Critical field for a second-order transition

The critical field H_m of the second-order transition to the TPS state, i.e., the field of formation of a superconducting nucleus, is found to be close to T_{c0} and it is obtained by solving the linearized Ginzburg-Landau equation corresponding to the highest temperature:

$$a\psi(\mathbf{r}) - \frac{1}{4m} \left(\nabla - \frac{2ie}{c} \mathbf{A} \right)^2 \psi(\mathbf{r}) = \gamma \delta(x) \psi(\mathbf{r}). \quad (4.17)$$

Equation (4.17) differs from the standard equation³¹ only by the presence of the δ function, i.e., it differs in respect of the boundary conditions $x = 0$ and, in order to stress this in our discussion, we shall not adopt dimensionless coordinates.

In the case of a type II superconductor the solution of Eq. (4.17) yields the true transition field, whereas for a type I superconductor the transition to the TPS state is of the second order only in the direct vicinity of the temperature T_c ; elsewhere throughout the temperature range of existence of the TPS the field H_m represents the field for supercooling of the normal phase.

The $H_m(T)$ curve lies somewhat above the dependence $H_{c2}(T)$, representing the upper critical field of a bulk metal given by $H_{c2} = \Phi_0/2\pi\xi^2(T)$ (Ref. 29), where $\Phi_0 = c\hbar/\pi e$ is a flux quantum and $\xi^2(T) = (\eta/4m)T_{c0}/(T_{c0} - T)$ describes the correlation length. The localized superconductivity in a field then exists in a type II superconductor at all temperatures (for the experimental data on the TPS in niobium see Sec. 3.3).

The situation is simplest in the case when the magnetic field is directed at right-angles to a twinning plane. In this case, selection of the vector potential gauge in the form $\mathbf{A} = [\mathbf{H} \times \mathbf{r}]/2$ and separation of the variables in Eq. (4.17) yields directly the solution in the form $\psi(r) = \varphi_0(\rho)f(x)$, where ρ is the coordinate in the (y, z) plane, $\varphi_0(\rho)$ is the standard⁵⁶ solution of Eq. (4.17) in the absence of the δ function, and $f(x)$ is the solution of Eq. (4.3) with the renormalized value of τ . Consequently, the temperature dependence $H_m^1(T) = 0.29(\Phi_0/\xi_0^2)(T_c - T)/T_{c0}$ differs from the usual dependence $H_{c2}(T)$ only by the fact that the field H_m^1 vanishes at the point T_c and not at T_{c0} . Therefore, the dependence $H_m^1(T)$ is a straight line passing through the

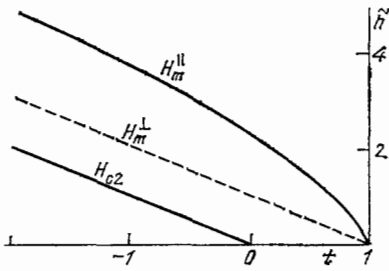


FIG. 10. Calculated dependences of the critical magnetic fields of a second-order phase transition in fields parallel and perpendicular to the twinning plane.^{11,16} Here, $\tilde{h} = H[(T_c - T_{c0})(dH_{c2}/dH)_{T_c - T_{c0}}]^{-1}$ and $t = (T - T_{c0})(T_c - T_{c0})^{-1}$.

point T_c and it is parallel to $H_{c2}(T)$ (Fig. 10).

The behavior of the TPS in a perpendicular field is such that near T_c it resembles the behavior of a thin superconducting plate of a type II semiconductor, for which the effective London penetration depth is given by^{31,61}

$$\lambda_{eff}^2 = \frac{16\pi e^2}{mc^2} \int \psi^2(x) dx,$$

and the role of the plate thickness d is played by the quantity

$$d \rightarrow \int \psi^2(x) dx (\psi^2(x=0))^{-1} \propto \xi(T_c).$$

When this replacement is done in the case of the TPS, all the results of Ref. 63 should apply, i.e., a vortex structure with the size of vortices $\xi(\tau_0)$ appears along the perpendicular field.

From the point of view of the fluctuation magnetism the TPS is also analogous to a thin superconducting film of thickness $\xi(T_c \sim \xi_0/\sqrt{\tau_0})$ and its fluctuation moment in a perpendicular magnetic field is proportional to $(T - T_c)^{-1}$ (Ref. 64). Such a temperature dependence of the fluctuations susceptibility typical of two-dimensional semiconductors should appear in the temperature range $(T - T_c)/T_c \lesssim \tau_0$. Experimental detection of the fluctuation diamagnetism of the TPS is obviously difficult because of the masking effect of bulk fluctuations and it is possible only in the case of samples with a high density of twinning planes.

The parallel field for a second-order transition to the TPS state $H_m^parallel$ can be found from the condition for the solution of the linearized equation of the order parameter (4.7), where \mathbf{A} is the vector potential of the external field and, instead of the boundary condition for φ , it is more convenient to introduce the δ potential into the equation:

$$-\varphi^parallel(x) + \tilde{h}^parallel x^2 \varphi(x) + t\varphi(x) - 2\delta(x)\varphi(x) = 0, \quad (4.18)$$

Here, $\tilde{h}^parallel = H_m^parallel/H_{c2}$ ($t = -1$) = $h/\sqrt{2}\xi$ and dimensionless coordinates are used.

The eigenfunctions $\varphi_n(x)$ of this equation without the δ function (i.e., of the linear oscillator equation) subject to the boundary conditions $\varphi \rightarrow 0$ at $x \rightarrow \pm\infty$ are well known⁵⁶ and they form a complete orthonormalized basis. We shall expand Eq. (4.18) in terms of these eigenfunctions:

$$\varphi(x) = \sum_n c_n \varphi_n(x). \quad (4.19)$$

Substituting Eq. (4.19) into Eq. (4.18) and using the orthonormalization condition of $\varphi_n(x)$, we find the coefficients

of the expansion

$$c_n = 2\varphi(0)\varphi_n(0)(t + \epsilon_n)^{-1}, \quad (4.20)$$

where $\epsilon_n = 2\tilde{h}^parallel(n + 1/2)$ is the eigenvalue of the energy corresponding to the function $\varphi_n(x)$. Using the "self-consistency" condition

$$\varphi(0) = \sum_n c_n \varphi_n(0),$$

and the explicit form of the functions $\varphi_n(x)$ (Ref. 56), we obtain the solution of our problem in the form of a converging series:

$$\begin{aligned} \tilde{h}^parallel^{1/2} &= \frac{2}{\sqrt{\pi}} \sum_{k=0}^{\infty} \frac{(2k)!}{(k!)^2 2^2 k [(t/\tilde{h}^parallel) + 4k + 1]} \\ &= \frac{1}{2\sqrt{\pi}} B\left(\frac{1 + (t/\tilde{h}^parallel)}{4}, \frac{1}{2}\right), \end{aligned} \quad (4.21)$$

where B is the beta function. Numerical summation of Eq. (4.21) gives the dependence $\tilde{h}^parallel(t)$ shown in Fig. 10.

In the limit $t \rightarrow 1$ the dependence $\tilde{h}^parallel(t)$ is of the square-root type $\tilde{h}^parallel(t) = [2(1-t)]^{1/2}$ and can easily be found if we consider the magnetic field in Eq. (4.21) as a perturbation.

In the limit $|t| \gg 1$ the critical field differs little from the corresponding exchange value $\tilde{h}_0 = H_{c2}/H_{c2}$ ($t = -1$) = $-t$: the sum of Eq. (4.21) may then be limited to just the first term with $k = 0$, which is much larger than the other terms. We consequently find that

$$\frac{h^parallel - \tilde{h}_0}{\tilde{h}_0} = \frac{H_m^parallel - H_{c2}}{H_{c2}} = \frac{2}{(\pi|t|)^{1/2}} \approx 1.1 |t|^{-1/2}, \quad (4.22)$$

$$\text{i.e., } \tilde{h}^parallel - \tilde{h}_0 = (2/\sqrt{\pi})|t|^{1/2}$$

In considering the behavior of the TPS in the range $|t| \gg 1$ in fields somewhat less than $\tilde{h}^parallel(t)$ we can use the traditional method⁶⁵ employed earlier in studies of the mixed state when fields are in the range $(H_{c2} - H)/H_{c2} \ll 1$ (see also Ref. 31). The mixed state is then characterized by a parameter $\beta_A = \bar{\varphi}^4/(\bar{\varphi}^2)^2$. In our case a vortex lattice does not appear and this parameter is even easier to find than in the case of a conventional bulk superconductor: instead of φ we have to substitute the eigenfunction of a linear oscillator [Eq. (4.18) without the δ function] corresponding to the lowest energy states. This gives

$$\beta_A = \left(\frac{|t|}{2\pi}\right)^{1/2} \frac{1}{\xi(\tau_0)},$$

so that the magnetic moment for the TPS has the following value per unit area

$$M_d = -\frac{H_m^parallel - H}{4\pi\beta_A(2\kappa^2 - 1)} = -\frac{(H_m^parallel - H)\xi(\tau_0)}{2(2\pi|t|^{1/2}(2\kappa^2 - 1))}. \quad (4.23)$$

This expression is valid if $H_m^parallel > H > H_{c2}$ and $|t| \gg 1$. An analysis of the relevant equation shows that on approach of the parallel field to H_{c2} there is no modulation of the solution along a twinning plane and this is true right up to $H = H_{c2}$.

The critical field for a second-order transition in the TPS case is characterized by a strong anisotropy (Fig. 10), which is manifested particularly clearly near the transition

temperature T_c : the perpendicular field depends linearly on temperature, whereas the parallel field obeys the square-root law. As pointed out before, the TPS near T_c behaves like a superconducting film of thickness $\xi(\tau_0)$. Therefore, the angular dependence of the field in the TPS case is identical with the angular dependence for a thin superconducting film⁶⁶ (see also Ref. 14):

$$\left| \frac{H_m(\theta) \sin \theta}{H_m^\perp} \right| + \left(\frac{H_m(\theta) \cos \theta}{H_m^\parallel} \right)^2 = 1, \quad (4.24)$$

where θ is the angle between the twinning plane and the field direction.

Far from the temperature T_c ($|t| \gg 1$) the excess of the TPS critical field above the value of \tilde{h}_0 for the bulk decreases quite rapidly from $\Delta \tilde{h}^\parallel$ to $\sim \Delta \tilde{h}^\perp$ when the field is tilted by an angle $\theta \propto \tilde{h}^{-1/4}$ from the parallel orientation.

Comparing the expressions for $\Delta \tilde{h}^\parallel$ and $\Delta \tilde{h}^\perp$ for $|t| \gg 1$, we find that the following ratio is obeyed

$$\frac{(\Delta H_m^\parallel)^2}{\Delta H_m^\perp H_{c2}} = \frac{4}{\pi}.$$

In the range of temperatures characterized by $t \approx 0$ an analysis of the TPS behavior in a field can be made only by numerical solution of Eqs. (4.7) and (4.8) for the order parameter and for a magnetic field parallel to a twinning plane.

Figure 11 illustrates the results of numerical calculations¹⁶ carried out for the case when $\kappa = 1$, which corresponds to niobium, at a temperature $t = -0.5$. Clearly, the magnetic field penetrates into the TPS region, which is typical of type II superconductors. The field dependence of the magnetic moment for $\kappa = 1$ (niobium) is in qualitative agreement with the experimental results in Fig. 7 and it is bell-shaped. The initial rise of the magnetization is due to an increase in the magnetic field; then, in stronger fields the superconductivity quenching effect begins and this is the reason for the fall of the magnetic moment on approach to the field H_m .

On the whole, this theoretical description is in qualitative agreement with the properties of the TPS of niobium (see Sec. 3.3). However, it follows from the experimental results that the value of dH_m^\parallel/dT at $T = T_{c0}$ exceeds dH_{c2}/dT by a factor of approximately 1.2, whereas the theoretical value of the ratio (Fig. 10) is about 1.5. The discrepancy is due to the fact that in the case of a second-order phase transition it is very difficult to determine experimentally the magnetic moment for the TPS (which is complicated even

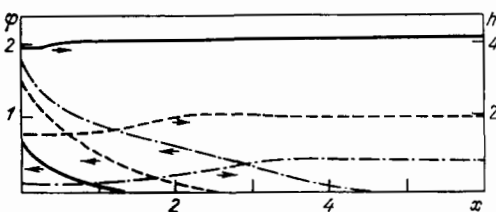


FIG. 11. Spatial dependence of the order parameter φ and screening of a magnetic field h parallel to a twinning plane of niobium ($\kappa = 1$) at a temperature $t = -0.5$ (Ref. 16). The continuous curve represents the field $h = \tilde{h}/\sqrt{2}\kappa = 4.2$, the dashed curve represents $h = 1.9$, and the chain curve represents $h = 0.71$. The coordinate x is measured in units of $\xi(\tau_0)$.

further by the inhomogeneity of a twinning plane) and the magnetic measurements essentially give only the lower limit for the field H_m . An important factor is also the need to ensure that the field is exactly parallel to a twinning plane. This may be the reason why the experimental data do not indicate any curvature of the dependence $H_m^\parallel(T)$. It should be pointed out that the strong nonlinearity of $H_m^\parallel(T)$ is expected in the limit $T \rightarrow T_c$, i.e., where measurements of the TPS magnetic moment are most difficult because of the vanishingly small value of this moment. Investigations of the angular dependence in a field $H_m(\theta)$ of niobium have not yet been carried out and the error of the experimental results is too large to check whether the dependence in Eq. (4.22) is obeyed.

In the case of tin ($\kappa = 0.13$) the transition to the TPS phase in a field is of the second order only in an extremely narrow interval near T_c . The reason for this change in the nature of the transition can be understood on the basis of the following considerations.

It is well known that the nature of the transition in conventional superconductors subject to a magnetic field is governed by the Ginzburg-Landau parameter $\kappa = \lambda_L/\xi$: if $\kappa > 1/\sqrt{2}$ the transition in a field is of the second order, whereas for $\kappa < 1/\sqrt{2}$ it is of the first order (see, for example, Ref. 55). As pointed out already in Sec. 4.2.1, in the case of the localized superconductivity the effective depth of screening of a field parallel to a twinning plane obeys $\lambda_{\text{eff}}^2 \propto \lambda_L^2(0)/\tau_0(1-t) \rightarrow \infty$ in the limit $t \rightarrow 1$. On the other hand, the superconducting correlation length for the localized superconductivity $\xi(T_c) \sim \xi_0/\sqrt{\tau_0}$ hardly changes near temperatures $T_c(t \rightarrow 1)$. Consequently, the effective Ginzburg-Landau parameter for the localized superconductivity depends strongly on temperature:

$$\kappa_{\text{eff}} \propto \frac{\lambda_L}{\xi_0} (1-t)^{-1/2} \propto \kappa (1-t)^{-1/2},$$

and diverges in the limit $t \rightarrow 1$. Near T_c the transition to the TPS phase in a field should therefore always be of the second order, irrespective of the nature of the superconductivity of the matrix. On the other hand, as temperature is lowered in a type I superconductor ($\kappa \ll 1$), the effective Ginzburg-Landau parameter approaches its value for a bulk metal when $1-t \gg \kappa^2$ and the transition should then be of the first order. Consequently, at some temperature t^* , such that $1-t^* \propto \kappa^2$, there should be a change in the nature of the transition occurring in a field parallel to a twinning plane. A rigorous analysis¹² shows that this change occurs at

$$t^* = 1 - 1.6\kappa^2. \quad (4.25)$$

In the case of tin we have $\kappa = 0.13$, so that the region where the transition is of the second order is vanishingly small.

In a perpendicular magnetic field the behavior of the TPS is, as pointed out already, analogous to the behavior of a thin superconductor film of thickness $d \sim \xi(T_c)$. Near the critical temperature T_c the superconductivity of a film subjected to a perpendicular field always appears as a result of a second-order phase transition.⁶³ It follows from Ref. 63 that the tricritical point of the TPS of a type I superconductor ($\kappa \ll 1$) obeys $(1-t) \propto \kappa^4$ and the region of a second-order transition it is even smaller than in a field parallel to a twinning plane.

4.2.3. Critical field for a first-order transition

In a type I superconductor characterized by $\kappa \gg 1$ the transition to the TPS phase should be of the first order throughout the temperature range of the existence of the localized superconductivity, exactly as in the bulk of the metal. If we now ignore the range of temperatures near the tricritical point t^* and consider the case of a field parallel to a twinning plane, we can ignore penetration of the field into the superconducting region near a twinning plane, as indicated by Eqs. (4.7) and (4.8) in the limit $\kappa \rightarrow 0$, and assume that the localized superconductivity exists in a layer of finite thickness $-L < x < L$, where there is no field, but the size of the localized superconductivity region still has to be determined. Essentially, we shall use Eq. (4.2) for φ , but with different boundary conditions: $\varphi(\pm L) = 0$. Inside the superconducting region the field and its vector potential vanish and the first integral of Eq. (4.9) allows us to write down the expression for the free energy of Eq. (4.1) (per unit area of the twinning plane) in the form

$$F = \xi(\tau_0) \frac{H_c^2(-\tau_0)}{8\pi} \left(\int_{-L/\xi(\tau_0)}^{L/\xi(\tau_0)} 2(\varphi')^2 dx - 2\varphi^2(0) \right). \quad (4.26)$$

It follows from the first integral of Eq. (4.9) that

$$\frac{d\varphi}{dx} = - \left(t\varphi^2 + \frac{\varphi^4}{2} + \frac{h^2}{2} \right)^{1/2}. \quad (4.27)$$

Allowing for the boundary condition which applies to φ on a twinning plane, we find from Eq. (4.27) that the relationship between the field h and the amplitude of the order parameter at $x = 0$ is given by

$$h^2 = 2(1-t)\varphi^2(0) - \varphi^4(0). \quad (4.28)$$

Applying once again Eq. (4.27) and going over from integration with respect to x to that with respect to φ in Eq. (4.26), we find from Eq. (4.27) that the free energy of the localized superconductivity can be described by

$$F = \varphi^2(0) \frac{H_c^2(-\tau_0)}{\pi} \times \left\{ \int_0^1 \left[1 - t(1-y^2) + \frac{1}{2}(y^4-1)\varphi^2(0) \right]^{1/2} dy - \frac{1}{2} \right\}. \quad (4.29)$$

The condition for a first-order transition $F = 0$ allows us to find implicitly the value of $\varphi(0)$:

$$\int_0^1 \left[1 - t(1-y^2) + \frac{1}{2}(y^4-1)\varphi^2(0) \right]^{1/2} dy = \frac{1}{2}. \quad (4.30)$$

so that using Eq. (4.28) we can now determine the field h_d . Equation (4.30) was solved numerically and the results are presented in Fig. 12. An important feature of the results is the intersection of the $h_d(T)$ and $h_c(T)$ curves, i.e., the localized superconductivity of a type I superconductor is limited to the range of temperatures near T_{c0} .

However, the error of these calculations is fairly large, of the order of $\kappa^{1/2}$, as is true of the case of the energy of a boundary between the superconducting and normal phases in a field (see, for example, Ref. 55). This is the reason for the discrepancy between the dependences $h_d(T)$ deduced

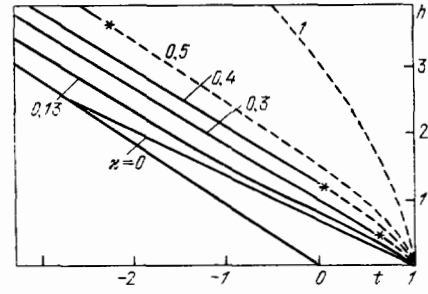


FIG. 12. Nature of the phase diagram of the twinning-plane superconductivity plotted for different values of κ in a parallel magnetic field near the temperature $t = 0$ (Ref. 16). The dashed curves are second-order transitions; the tricritical points corresponding to a change in the nature of the transition are identified by asterisks.

from Eqs. (4.28) and (4.30), on the one hand, and the experimental results, on the other.

The size of the localized superconductivity region is of the order of $\xi(\tau_0)$ and it can be readily found from Eq. (4.27):

$$\frac{2L}{\xi(\tau_0)} = \int_0^{\varphi(0)} \frac{d\varphi}{[t\varphi^2 + (\varphi^4/2) + (h^2/2)]^{1/2}}. \quad (4.31)$$

Since the field is expelled completely from the localized superconductivity region, its magnetic moment (per unit area) is $M_d = -HL(H)/2\pi$.

In comparing the theory with experimental results on the TPS in tin, a numerical solution was obtained of Eqs. (4.7) and (4.8) and this was done by the method of finite differences in the case when $\kappa = 0.13$, which corresponds to tin.¹⁶ We can see from Fig. 6 that a very good quantitative agreement with the experimental results is then obtained.

We must stress once again that the phase diagram shown in Fig. 6 was calculated without recourse to any fitting parameters.

As pointed out already, the inhomogeneity of a twinning plane does not interfere with the determination of the first-order transition field H_d , but the abrupt change of the moment at $H = H_d$ is no longer observed. This jump in the moment appears because of "supercooling" in a field of the normal phase down to the field $H = H_m$ (which is the absolute instability field for the normal state and it corresponds to a second-order transition, see Sec. 4.2.2) and this makes it possible to determine the field H_m for tin (see Sec. 3.2). The experimental dependence $H_m(T)$ for tin shown in Fig. 5 has the slope -30 Oe/K, which is only slightly higher than the slope $dH_{c2}/dT = -30$ Oe/K for the bulk material. The theoretical dependence $H_m(T)$ for the parallel field at $T = T_{c0}$ should then have the slope ~ -45 Oe/K; it lies above the experimental curve. This may be due to indeterminacy of the orientation of the field relative to a twinning plane (so that the experimental dependence lies between H_m^\perp and H_m^\parallel) as is true of niobium.

It follows from the theoretical and experimental investigations that the TPS of tin may be observed only in the temperature range $-(6-7) < t < 1$, i.e., at temperatures $T_{c0} - 0.25$ K $< T < T_{c0} + 0.04$ K. The lower limit to the temperature range of the existence of the TPS is specific to type I superconductors and is due to the fact that cooling in

the TPS state results in a loss of the inhomogeneity energy which exceeds the gain in the energy of the superconducting condensation near a twinning plane.

The narrow temperature range of the existence of the TPS in type I superconductors makes it possible to describe fully this phenomenon using the Ginzburg-Landau approach. In type I superconductors the conditions of validity of the Ginzburg-Landau theory are however quite stringent: all the parameters of the system including the magnetic field should vary slowly over distances of the order of ξ_0 . In our case the depth of penetration of the field is $(\lambda_L \xi)^{1/2}$ and it is greater than λ_L because $\varphi(x)$ vanishes at the boundary with a normal metal (a similar situation occurs in the case of the N/S interface in a type I superconductor⁵⁵). Consequently, the condition of validity of the Ginzburg-Landau theory needed for a complete description of the localized superconductivity of a type I superconductor is $\tau_0 < \kappa^{1/2}$, which is satisfied for the TPS of tin.

The nature of the behavior of the order parameter and of the screening of the field as a function of the coordinates in tin is illustrated in Fig. 13. It is interesting to note that in the range of negative values of t , when in weaker fields we can expect bulk superconductivity, on approach of the field to $h_c = -t$ it is found that the dependence $\varphi(x)$ exhibits a plateau where the order parameter remains practically constant and equal to its value for a bulk metal at a given temperature. The inhomogeneity of a real twinning plane has the effect that the experimental values of the magnetic moment are approximately an order of magnitude less than the theoretical values and there is no abrupt change in the magnetic moment in a field $H = H_d$. A strong nonlinearity of the dependence $M_d(H)$ is related to a reduction in the localized superconductivity region on increase in the field.

The phase diagram of the TPS for superconductors of extreme type I ($\kappa = 0$) and for type II superconductors is relatively simple. However, if κ is finite, then the (H, T) phase diagram of the TPS can be found only by numerical methods. The results of such numerical calculations are presented in Fig. 12.

We recall that in the case of type I superconductors the appearance of the TPS in a field just below the temperature T_c always takes place by a second-order phase transition (see Sec. 4.2.2). At the tricritical temperature T^* [$(T_c - T^*)/(T_c - T_{c0}) = t^*$; see Eq. (4.25)] there is a change in the nature of the transition from the second to the first order. It is clear from Fig. 12 that as κ increases, the range of the second-order transition widens and the tem-

perature T^* decreases. The dependence $H_d(T)$ then becomes steeper and the range of existence of the TPS widens in the direction of lower temperatures.

In a perpendicular magnetic field one would expect an intermediate state in a type I superconductor. The problem of the structure of the intermediate state in the TPS case when a field is perpendicular to the plane differs from its usual formulation for a thin superconductor plate and it has not yet been solved finally. The critical field for a first-order transition perpendicular to a twinning plane is of the same order of magnitude as the parallel field. However, it is clearly slightly less than the parallel field, because the structure of the intermediate state which then appears should have a nonzero demagnetization factor. This is the difference between the TPS and the conventional case of a film of a type I superconductor where the critical field is independent of the relative orientation of the field and the film.

We shall conclude this section by noting that a twinning plane affects also the surface superconductivity field H_{c3} . If this plane is parallel to the surface of a sample, the influence of the surface on the critical temperature of the TPS may be important at distances between the twinning plane and the surface amounting to $L \propto \xi(\tau_0)$. In this case the proximity effect is weakened to one side of the twinning plane and for $L \ll \xi(\tau_0)$ the critical temperature obeys $(T_c - T_{c0})/T_{c0} \rightarrow 4\tau_0$. In a parallel magnetic field a superconducting nucleus appears always at the surface of a homogeneous superconductor.³¹ The TPS alters the situation: in weak fields the nucleation of the superconductivity always occurs at a twinning plane, but on increase in the field the nature of localization of the superconductivity changes and the appearance of the surface superconductivity is preferred (the relevant field is governed by the distance between the twinning plane and the surface). Consequently, a kink may appear in the temperature dependence of the supercooling field (in the case of a type I superconductor). In fact, the supercooling field near T_c is the field H_m , whereas at lower temperatures it is H_{c3} . An increase in the field H_{c3} should occur also in the case of a perpendicular orientation of a twinning plane relative to the surface of a sample. A more detailed discussion of this topic can be found in Ref. 76.

Experiments have revealed that some metals are characterized by surface superconductivity fields exceeding $H_{c3} = 1.69H_{c2}$ (Refs. 77 and 78). The role of twinning planes, which appear readily near the surface during processing, has been ignored. However, a twinning plane may appear at the surface of niobium during its rolling and it is reported in Ref. 79 that the field H_{c3} increases as a result of rolling of niobium.

5. TWINNING-PLANE SUPERCONDUCTIVITY IN THE "ABSENCE" OF THE PROXIMITY EFFECT

5.1. Experiments

We have pointed out already that the small difference between the temperatures T_c and T_{c0} is largely determined by the proximity effect. Bearing in mind that the observed effective thickness of the superconducting layer is of the order of ξ_0 (which amounts to a few thousands of angstroms for tin) and that the thickness of a layer near a twinning plane where there is a change in the electron-phonon characteristics does not exceed several interatomic spacings, we

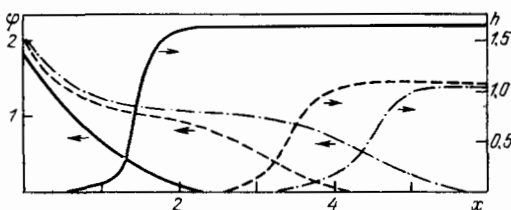


FIG. 13. Spatial dependence of the order parameter φ and screening of a magnetic field h parallel to a twinning plane of tin at the temperature $t = -1$ (Ref. 16). The continuous curve corresponds to an external field $h = 1.62$, the dashed curve corresponds to $h = 1.05$, and the chain curve corresponds to $h = 1.011$. The coordinate x is measured in units of $\xi(\tau_0)$.

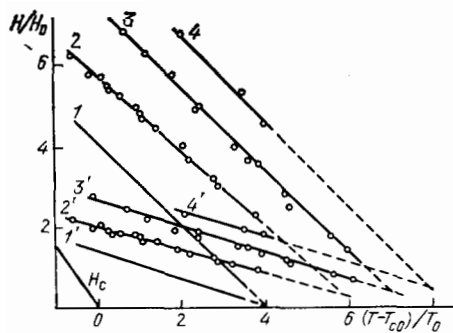


FIG. 14. Phase diagram of the twinning-plane superconductivity of tin in the case of closely spaced twinning planes: 1), 1') isolated twinning plane, shown for comparison; 2), 2') separation between twinning planes 3×10^{-3} cm; 3), 3') separation 3×10^{-4} cm; 4), 4') separation 10^{-4} cm.

can see that the recorded change in the critical transition temperature, of the order of 0.04 K for tin, is in fact extremely large, i.e., the critical temperature which would have been observed in the absence of the proximity effect exceeds considerably the critical temperature of a single crystal of the same metal. The influence of the proximity effect cannot be excluded completely, but it can be largely weakened by placing several twinning planes relatively close to one another or removing the normal metal surrounding a twinning plane.

Experiments on tin samples containing several twinning planes demonstrated that the dependences $M_d(T, H)$ remain qualitatively the same. As in the case of an isolated twinning plane, the transition to the TPS state in tin is of the first order. The dependences $M_d(H)$ measured at fixed temperatures can be used to find the critical magnetic fields H_c , H_d , and H_m .

The results of measurements of the critical magnetic fields of tin samples with several closely spaced twinning planes are presented in the phase diagram in Fig. 14. This (H, T) phase diagram is plotted using the following normalized coordinates: $(T - T_{c0})/T_0$ along the temperature axis and H/H_0 along the magnetic field axis. This diagram shows the $H_c(T)$ line as well as, for the sake of comparison, the lines of the critical magnetic fields of an isolated twinning plane $H_d(T)$ and $H_m(T)$ taken from the phase diagram in Fig. 5 and denoted here by 1 and 1'. The results represented by the lines 2 and 2' and also by 3 and 3' were obtained in an investigation of samples with two twinning planes oriented parallel to one another and separated by distances of 3×10^{-3} and 3×10^{-4} cm, respectively. The presence of two twinning planes was confirmed and the distance between them was measured with the aid of an optical microscope after the sample was etched, which revealed its crystal structure.

The diamagnetic moment M_d determined in weak fields (weaker than H_m) at the reference temperature T_{c0} for samples with two closely spaced twinning planes was twice as large as the diamagnetic moment for samples with one twinning plane. In weak fields the proportionality of M_d to the twinning plane area made it possible to estimate, at least in the first approximation, the total area of a twinning plane when the number and orientation of twinning planes in a sample could not be determined by other methods. The need for such an estimate arises, for example, in studies of samples in which twinning planes distributed randomly throughout a

sample are created as a result of strong plastic deformation.

Lines 4 and 4' represent the results obtained for a sample in which the density of twinning planes estimated from the amplitude of the diamagnetic moment M_d was of the order of 10^4 cm²/cm³, which corresponded to an average distance between twinning planes of the order of 10^{-4} cm. Such a density of twins was obtained as a result of homogeneous plastic deformation of a sample of tin when its linear dimensions changed by 2–50%. Annealing of a deformed sample had practically no effect on the recorded dependences $M_d(T, H)$.

A comparison of the phase diagram in Fig. 14 (lines 1 and 1') with the phase diagram in Fig. 5 demonstrated that the influence of the proximity effect in a sample with several twinning planes was indeed weakened and the range in which the TPS was observed became considerably wider. All the relationships between the parameters characterizing the TPS and described by Eq. (3.2) were still obeyed, with the exception of the third one, which should include the dependence on the distance between twinning planes. The problem of the dependence of T_c on the distance between twinning planes will be discussed in the second part of the present section, which provides a theoretical description of twinning planes interacting with one another. To an order of magnitude, we can say that the approach of twinning planes to a distance $\sim \xi$ doubles the temperature difference $T_c - T_{c0}$ compared with the corresponding difference for the isolated twinning plane.

It is worth noting that the points of intersection of the H_d and H_m lines in the phase diagram of Fig. 14 are located systematically above the temperature axis. According to the theory put forward above (see Sec. 4.2.3) an increase in temperature should change the order of the thermodynamic normal-TPS transition from the first to the second. The point of intersection of the lines H_d and H_m may be the theoretically predicted tricritical point. Unfortunately, the sensitivity of the magnetometer used in Ref. 4 was insufficient to investigate the properties of the TPS in this very interesting region.

The presence of twin boundaries in a density of 10^4 cm²/cm³ in a sample affects its electrical resistance. A reduction in the resistance of such samples under external conditions corresponding to the observation of M_d was reported in Ref. 37.

The next stage in the attempt to increase the density of twins in a sample can be made by concentrating on an increase in the number of twin boundaries in just one part of a single crystal. It is known that surface treatment of materials (such as grinding) induces plastic deformation in a relatively thin layer near the surface. A study of the properties of twins formed in the surface layer of tin was reported in Ref. 5.

The samples used in this study⁵ were formed in the course of grinding of the surface of a single crystal of tin with a corundum powder consisting of grains of 10 μ m approximate size. Etching of these samples revealed that the surface layer had a fine-grained structure. The thickness of this fine-grained layer was approximately 50 μ m, as found by electrochemical etching.

Figure 15 shows the magnetic-field dependences of the magnetic moment determined at three different temperatures for such samples. The curve at the top of the figure, recorded at a temperature which was 0.044 K higher than

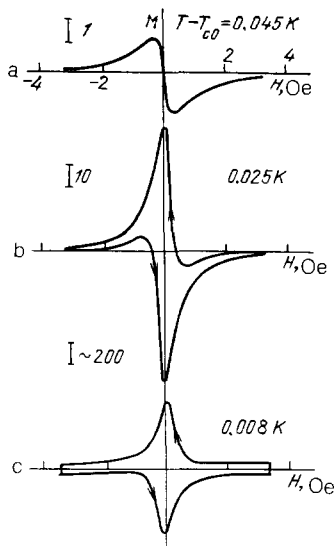


FIG. 15. Magnetic-field dependences of the magnetic moment of samples of tin with an average distance of the order of 10^{-5} cm between twinning planes.² The hysteresis manifested above is due to the appearance of non-decaying currents flowing along a macroscopic circuit.

T_{c0} , revealed clearly a diamagnetic moment M_d . The temperature of the appearance of M_d determined in these experiments was higher than in all the other experiments discussed in the present paper. However, the error in the determination of the critical temperature of the TPS was fairly large. This was due to the absence of clear overheating-supercooling phenomena. Judging by the temperature of appearance of the diamagnetic moment M_d , it was concluded that the critical temperature T_c of the TPS was at least 0.1 K higher than the critical temperature of the bulk superconductivity T_{c0} .

Layer-by-layer electrochemical etching revealed that most ($\sim 90\%$) of the twins created by grinding were concentrated in a layer of thickness $5\text{--}6\ \mu\text{m}$ and the average distance between the twins deduced from the diamagnetic moment M_d was $\sim 10^{-5}$ cm.

Cooling of such samples created favorable conditions for the flow of a nondecaying electric current throughout the layer enriched with twins. The appearance of a nondecaying current flowing in a circuit of macroscopic dimensions was manifested in magnetic measurements by hysteresis loops of the dependences $M(H)$. All the curves (the average ones are shown in Fig. 15) were similar to the dependence $M(H)$ obtained for niobium at temperatures $T_{c0} < T < T_{c1}$ (Fig. 7). It was interesting that the conditions favoring the appearance of macroscopic nondecaying currents were obtained when the "effective" thickness w of the superconducting layer near a twinning plane exceeded the average distance between twin boundaries.

A further cooling right down to T_{c0} increased the critical current flowing through the superconducting layer and the magnetic moment of this current exceeded considerably the diamagnetic moment M_d . The dependences $M(H)$ assumed the form shown in the lowest graph in Fig. 15. The high values of the magnetic moment of the current circulating along a macroscopic circuit made it possible to check that there was no decay of this current. It was found that the magnetic moment (and, therefore, the current) remained

constant for ~ 5 h and this was accurate to within $\sim 1\%$.

The experiments involving layer-by-layer electrochemical etching made it possible to estimate the critical current density for the layer rich in twins. It was found that this critical density reached $j \approx 16^6$ A/cm² at $T = T_{c0}$ for $H = 0$.

In spite of the fact that changes in the nature of the dependences $M(H)$ in Fig. 15 were fully analogous to the changes in the dependences in Fig. 7, there was a considerable difference between these two experiments. In the case of niobium a sample contained only one twinning plane, but nevertheless a nondecaying current could flow along this plane. In the case of tin a macroscopic superconducting current flowed only when a relatively thick ($> 1\ \mu\text{m}$) layer with a high density of twins was formed. An isolated twinning plane in tin always had a finite resistance at temperatures $T > T_{c0}$. For this reason the appearance of currents in macroscopic circuits could be regarded as a topological Berezinskii-Kosterlitz-Thouless phase transition only in the case of niobium. Macroscopic nondecaying currents flowing in a three-dimensional network of twins in tin were most probably of different origin.

Experiments on samples containing several twinning planes confirmed that the small difference between the critical temperatures of the TPS and of the bulk superconductivity was due to the proximity effect. It was possible to reduce the influence of this effect by forming several twinning planes quite close to one another. There is as yet no technology which would make it possible to prepare samples in which twinning planes would be separated by distances of the order of tens of angstroms. For this reason it is not possible to determine experimentally the "true" critical temperature of the TPS unaffected by the proximity effect. All that we can say is that the "true" critical temperature of the TPS is considerably greater than T_{c0} .

Another important observation made in a sufficiently dense three-dimensional system of twins was the flow of a nondecaying electric current with a high density over macroscopic distances. The experiments on nondecaying currents in macroscopic circuits confirmed that this effect should indeed be regarded as the TPS.

As pointed out earlier, the proximity effect can be weakened also in the case of a sample with a thin (of thickness less than ξ_0) bicrystal layer in which a twinning plane is parallel to the surface of the layer. A method which could be used to produce such samples is not yet known. However, a sample in which a twinning plane is surrounded by a small amount of a normal metal in a region with characteristic size less than ξ_0 is feasible. The situation occurs if a sample is in the form of a fine-grained powder with the required particle size. Some of the powder particles are twins directly after preparation; moreover, the concentration of bicrystal twin particles can be increased by subjecting the powder to plastic deformation at low temperatures.

Samples consisting of fine particles of pure tin prepared by two methods were used in Ref. 5. In the first case, an aggregate of particles of size $1.0\text{--}10\ \mu\text{m}$ was formed on the surface of a single crystal of tin as a result of spark machining of this crystal. The thickness of the layer of particles was then several tens of microns. In the second case, samples were pellets compacted from a powder at liquid nitrogen temperature until the density of a pellet reached $6\ \text{g/cm}^3$;

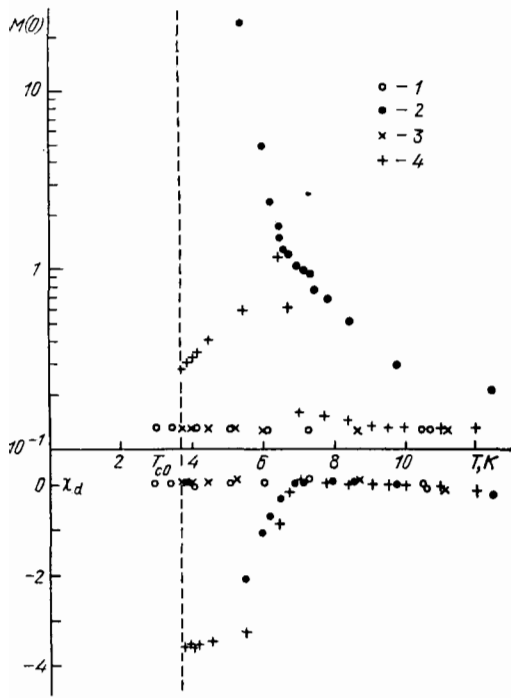


FIG. 16. Temperature dependences of the magnetic moment of tin microparticles at $H = 0$ and of their diamagnetic susceptibility⁵: 1) control run of a magnetometer in the absence of a sample; 2) microparticles on the surface of a single crystal; 3) powder of microparticles before compacting; 4) after compacting.

typical dimensions of the particles were the same as before. The volume of a pellet was about 1 mm^3 .

Determination of the magnetic moment of one of the microparticles of tin demonstrated⁵: 1) a hysteresis of the dependence $M(H)$, which could be described conveniently by its amplitude $M(0)$ in zero magnetic field; 2) a relatively high diamagnetism of the samples.

The results of a determination of the magnetic moment $M(0)$ and of the magnetic susceptibility χ_d as a function of temperature are presented in Fig. 16. The points representing the results of measurements of the magnetic susceptibility at temperatures 3.72 K are not included in Fig. 16: they lie well below the edge of the figure. Therefore, the dependence $\chi_d(T)$ obtained for the investigated samples has two steps: one of them (the larger) is located at 3.72 K and the other (the smaller) is broader and occupies the temperature interval from 6 to 7 K. Assuming that the magnetic susceptibility of the particles in the superconducting state is $-1/4\pi$, we find that a comparison of the step heights on the dependence $\chi_d(T)$ can be used to estimate the number of particles in which twins would appear in the process of preparation of the samples. According to these estimates the concentration of particles with twins was $\sim 10^{-4}$. Control measurements of the dependences of the magnetic susceptibility of tin powder before the compacting procedure demonstrated the presence of just one step at $T = 3.72 \text{ K}$. This result indicated that our material was chemically pure and that the concentration of twinned particles in the original sample did not exceed 10^{-5} . The fact that the superconductivity of particles with twins occurred in a fairly wide range of temperatures ($\sim 1 \text{ K}$), could be attributed to the scatter of the dimensions of the particle powder by more than one order of magnitude.

At temperatures below 3.72 K the dependences $M(H)$ exhibited a hysteresis with an amplitude that decreased strongly at temperatures 6–7 K but did not disappear completely, at least up to $\sim 12 \text{ K}$. This observation should be attributed to the presence of a small (in a concentration of 10^{-5} – 10^{-6}) amount of multiply twinned particles. The presence of nondecaying electric currents was particularly strongly manifested in the experiments on layers of particles on the surface of a single crystal. It should be pointed out that in such a tiny amount of a material the superconductivity of a twinning plane could not be detected from changes in the magnetic susceptibility.

Experiments on microparticles clearly demonstrated that the critical temperature of the transition of a twinning plane in tin to the superconducting state in the absence of the proximity effect is very high, at least 12 K, which is over three times the critical transition temperature for a single crystal. It should be pointed out that similar experiments on microparticles were reported earlier^{67, 69}; it was found that the diamagnetic component of the susceptibility of the samples of tin was observed at temperatures ~ 5 – 6 K . The authors of these investigations attributed the increase in the critical temperature to the influence of the surface on the superconducting properties of microparticles and they did not consider twinning as a possible reason for the change in the critical temperature.

5.2. Theory

Experiments confirmed directly weakening of the proximity effect and an increase in the critical temperature T_c in the presence of a number of closely spaced twinning planes. We shall calculate T_c for a periodic sequence of twinning planes (this case corresponds also to a layer of thickness equal to the period of a sequence in the middle of which a twinning plane is located) and two closely spaced twinning planes. The critical temperature can be found if we obtain the solution of the linearized equation (4.5).

We shall first consider a periodic (with a period L) sequence of twinning planes. In this case we have to find the periodic solution for $\varphi(x)$ and clearly at $\varphi(x)$ we have a minimum halfway between the twinning planes, i.e., $\varphi'[Ln + (L/2)] = 0$, where $n = 0, \pm 1, \pm 3, \dots$ (twinning planes occur at the coordinates $x_n = nL$). It follows from the formulation of the problem that we need to consider only section $-L/2 < x < L/2$ with the following boundary conditions for the function φ : $\varphi'(\pm L/2) = 0$. It is quite obvious that this situation is identical with that of finding T_c in a layer of thickness L containing a twinning plane (the boundary conditions $\varphi'(\pm L/2) = 0$ are satisfied at the superconductor-vacuum interface³¹).

The general solution of the linearized equation (4.5) is

$$\varphi(x) = A \exp(-t^{1/2} |x|) + B \exp(t^{1/2} |x|). \quad (5.1)$$

The boundary conditions $|\varphi'(0)| = \varphi(0)$ and $\varphi'(L/2\xi(\tau_0)) = 0$ make it possible to find separately the ratio of the coefficients A/B and then the compatibility condition determines implicitly the critical temperature:

$$\frac{L}{\xi(\tau_0)} = \frac{1}{t^{1/2}} \ln \frac{t^{1/2} + 1}{t^{1/2} - 1}, \quad (5.2)$$

which shows that in the two limiting cases we have

$$t = 1 + 4 \exp\left(-\frac{L}{\xi(\tau_0)}\right) \quad \text{for } L \gg \xi(\tau_0),$$

$$t = \frac{2\xi(\tau_0)}{L} \quad \text{for } L \ll \xi(\tau_0). \quad (5.3)$$

The condition of validity of our analysis is $L \gg \xi_0$, which ensures that the Ginzburg-Landau equations are satisfied. If $L \ll \xi_0$, we have to carry out an analysis of the integral equation for the order parameter. In the first approximation, the critical temperature is governed by the average value of the Cooper pairing constant (Refs. 70 and 71) which in the case of a twinning plane in tin should increase considerably the value of T_c compared with T_{c0} .

Unfortunately, as pointed out already, there is as yet no technology for the fabrication of samples with a periodic sequence of twinning planes and, from the point of view of a comparison with the experimental results, it would be of considerable interest to analyze the situation with two closely spaced twinning planes. If twinning planes are located at $x = \pm L/2$, we have to solve Eq. (4.5) subject to the boundary conditions $\varphi(\pm\infty) = 0$ and $\varphi'(0) = 0$. The order parameter reaches its maximum halfway between the twinning planes. The relationship between the critical temperature and the separation between twinning planes is then given by the relationship

$$\frac{L}{\xi(\tau_0)} = \frac{1}{t^{1/2}} \ln \frac{1}{t^{1/2} - 1}. \quad (5.4)$$

If $L \ll \xi(\tau_0)$, we find that $t \rightarrow 4$, i.e., the difference $T_c - T_{c0}$ for two closely spaced twinning planes increases by a factor of 4. This result corresponds to the dependence (see Sec. 4.2.2) for the microscopic model: we then have $\delta\lambda \rightarrow 2\delta\lambda$.

In the case of small samples with dimensions less than ξ_0 , the influence of a twinning plane on the superconductivity also increases: in this case the critical temperature is determined by the volume-averaged Cooper pairing constant.⁶ For example, in the case of spheres with a central twinning plane and a radius $R \ll \xi_0$, the average value is

$$\bar{\lambda} = \lambda_0 + \frac{3}{4} \frac{\Lambda}{R}.$$

If we assume that $(\bar{\lambda} - \lambda_0)/\lambda_0 \ll 1$, we readily obtain the dependence of the critical temperature of the spheres T_{cR} on

their size:

$$\ln \frac{T_{cR}}{T_{c0}} = 1,2 \frac{\xi_0}{R} \left(\frac{T_c - T_{c0}}{T_{c0}} \right)^{1/2}. \quad (5.5)$$

We can check this dependence by experiments on spheres separated in accordance with their size. The rise of T_{cR} on reduction of the sphere radius is limited to the size quantization effects.⁷² An estimate shows that in the case of tin this corresponds to $R \lesssim 100 \text{ \AA}$. However, for even larger values $R \sim 200\text{--}400 \text{ \AA}$ the effective constant $\bar{\lambda}$ becomes of the order of unity (when the weak coupling approximation no longer applies). Therefore, we can exclude the possibility that in the case of small tin particles with the twinning plane we can have a situation characterized by $\bar{\lambda} \sim 1$, which should correspond to an increase in T_c by almost an order of magnitude compared with T_{c0} .

6. TWINNING IN HIGH-TEMPERATURE SUPERCONDUCTORS

Until recently the highest superconducting transition temperatures have been of the order of $\sim 20 \text{ K}$ and these have been observed for compounds of the A-15 type. It is interesting to note that all these compounds exhibiting superconductivity are also characterized by a structural transformation of the martensitic type.⁸⁰ This transformation creates a highly developed twinning structure giving rise to polysynthetic twins.²⁵ In the case of Nb_3Sn a typical distance between twinning planes^{81,82} is $50\text{--}100 \text{ \AA}$. It would be of interest to consider the influence of twinning planes on superconducting properties of compounds of this type.

The martensitic transformation occurs also in high-temperature ($T_c \sim 95 \text{ K}$) superconductors of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ type. Polysynthetic twins created by the martensitic transformation form regular lattices with the twinning plane (110) and with the distances between twinning planes ranging⁸³⁻⁸⁶ from 200 \AA to 2000 \AA . A structural martensitic transformation in high-temperature superconductors occurs at approximately 700°C and the lattice symmetry then changes from tetragonal to orthorhombic.

It is reported in Ref. 87 that a square-root temperature dependence, of the type described by Eq. (4.21) (see Fig. 10), of the critical field parallel to a twinning plane was observed for oriented $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ crystallites. This was attributed in Ref. 87 to the appearance of the TPS in YBa_2Cu_3

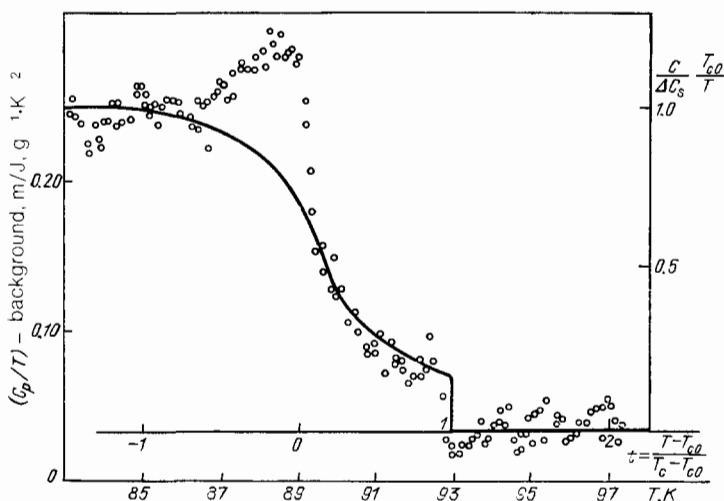


FIG. 17. Temperature dependence of the specific heat near the superconducting transition in a $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystal plotted on the basis of Ref. 89 (symbols). The continuous curve represents the results of a theoretical calculation⁹⁰ of the temperature dependence of the specific heat $C(T)$ of a system of parallel twinning planes separated by a distance $L/\xi(\tau_0) = 12$; here, $\Delta C = 1/\eta^2 b T_{c0}$ is an abrupt change in the specific heat due to the bulk superconducting transition in the absence of a twinning plane.

$O_{7-\delta}$. The distance between the twinning planes in the crystals investigated in Ref. 87 was 1270–1400 Å, which was considerably greater than the superconducting correlation length of high-temperature superconductors, so that the interaction between twinning planes could be ignored. It follows from the data of Ref. 87 and from the dependence (4.21) (when use is made of the results of measurements of the bulk critical field parallel to the c axis in $YBa_2Cu_3O_{7-\delta}$ single crystals⁸⁸: $dH_{c2}/dT \approx 1$ T/K) that $T_c - T_{c0} \approx 5$ K and $T_{c0} \approx 87$ K.

The presence of twinning planes in high-temperature superconductors of the $YBa_2Cu_3O_{7-\delta}$ type thus increases the critical temperature by about 5%.

Precision measurements of the specific heat of $YBa_2Cu_3O_{7-\delta}$ single crystals⁸⁹ demonstrated two anomalies: a weak one at 93 K and a much stronger one at 89 K. The results of Ref. 89 were in agreement with the concept of the TPS at $T_c \approx 93$ K and they indicated that the bulk superconducting transition occurred at $T_{c0} \approx 89$ K.

Equation (4.2) for the superconductivity parameter was solved in Ref. 90 for a periodic sequence of twinning planes and the temperature dependence of the specific heat was determined for such a system. The results of the calculations carried out for a sequence of twinning planes with a period $L/\xi(\tau_0) = 12$ ($L \sim 1200$ Å) are plotted in Fig. 17 alongside the experimental data of Ref. 89. The experimentally observed small peak of the specific heat near the temperature T_{c0} was clearly due to fluctuation effects.

In the case of closely spaced twinning planes separated by $L < \xi(\tau_0)$ we could expect an increase in the critical temperature because of weakening of the proximity effect (see Sec. 5). The short superconducting coherence length of high-temperature superconductors makes this mechanism effective for distances between twinning planes less than 100 Å. The superconductivity at temperatures above 100 K may be due to the appearance of a small-scale twinning structure in such samples.⁹⁰

We should also mention the possibility of an exotic twinning-plane superconductivity⁹¹ in which the phase of the superconductivity order parameter differs by π on each side of a twinning plane.

7. CONCLUSIONS

The investigations reviewed above have revealed (and provided some information on) the new phenomenon of twinning-plane superconductivity. This superconductivity is clearly one of the first manifestations of the special properties of electrons and phonons in systems of this kind revealed by current investigations.

It must be stressed that in all the experiments described above a direct study has been made not of the properties of quasiparticles in a twinning plane but of changes in the superconducting properties of a layer of an ordinary three-dimensional metal adjoining a twinning boundary and affected by it. The presence of a twinning boundary seems to favor the superconductivity in the surrounding layer of a normal metal.

The situation becomes more complex because in the investigated samples (Sec. 2) the average distances between defects on a twinning plane are considerably less than the distances typical of the superconductivity (see, for example,

λ_L and ξ_0). The experimental data available at present are insufficient to distinguish the influence of a twinning plane itself and of its defects on the conditions of appearance of the TPS. Further investigations are needed before such a distinction can be made.

The indeterminacy of the region for the enhancement of T_c near a twinning plane does not prevent a theoretical analysis of the phase diagram of the TPS. The theoretical approach developed so far makes it possible to plot the (H, T) phase diagram without any fitting parameters and such a diagram is in good agreement with the experimental results.

The problems of the mechanism of the superconductivity of a twinning plane, the existence of two-dimensional quasiparticles with twinning planes, and role of the defects of twinning planes will have to be tackled in order to gain a fuller understanding of the TPS. Unsolved problems make it urgent to study twinning planes.

It would therefore be very interesting to investigate, by a great variety of modern methods, the microscopic characteristics of twinning planes (quasiparticle spectra and the structure of twinning planes) and also to develop a microscopic theory of the TPS including numerical calculations of the electron and phonon characteristics of a twinning plane. Moreover, it would be undoubtedly of interest to study the properties of twins with high crystallographic indices of the twinning plane.

Finally, the presence of twins (when the density of twins is high or the particles are small) may increase considerably the critical temperature of the superconducting transition. When the technological problem of creation of synthetic structures based on twins is solved, new ways of obtaining superconductivity with extremely high critical parameters may open up. There is no doubt that, in addition to the TPS, it will be found that there are other phenomena which appear due to the existence of twinning planes.

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¹It should be noted that we investigated only the twins with the minimum possible energy of a twinning plane, but it would be of interest to study also the twinning-plane superconductivity in the case of higher crystallographic indices of the twinning planes.

²In particular, the proposed functional should describe the localized superconductivity which appears when a material with a higher critical temperature is deposited on a superconductor. It should also be noted that a similar functional has been used earlier to describe surface magnetic and structural transitions.^{74,75}

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